DTU Library

Risk assessment models and uncertainty estimation of groundwater contamination from point sources

Troldborg, Mads

Publication date:
2010

Document Version
Publisher's PDF, also known as Version of record

Link back to DTU Orbit

Citation (APA):
Troldborg, M. (2010). *Risk assessment models and uncertainty estimation of groundwater contamination from point sources*. Technical University of Denmark.

Technical University of Denmark

Risk assessment models and uncertainty estimation of groundwater contamination from point sources

Mads Troldborg

DTU Environment
Department of Environmental Engineering

PhD Thesis
July 2010

Risk assessment models and uncertainty estimation of groundwater contamination from point sources

Mads Troldborg

PhD Thesis
July 2010

DTU Environment
Department of Environmental Engineering
Technical University of Denmark

Mads Troldborg

Risk assessment models and uncertainty estimation of groundwater contamination from point sources

PhD Thesis, July 2010

The thesis will be available as a pdf-file for downloading from the homepage of the department: www.env.dtu.dk

Address:	DTU Environment Department of Environmental Engineering Technical University of Denmark Miljoevej, building 113 DK-2800 Kgs. Lyngby Denmark
Phone reception:	+45 4525 1600
Phone library:	+45 4525 1610
Fax:	+45 4593 2850
Homepage:	http://www.env.dtu.dk
E-mail:	reception@env.dtu.dk

Printed by:	Vester Kopi Virum, July 2010
Cover:	Torben Dolin
ISBN:	978-87-92654-05-2

Preface

This PhD thesis is based on research undertaken from October 2006 to May 2010 at the Department of Environmental Engineering, Technical University of Denmark (DTU). The work was done under the supervision of Associate Professor Philip J. Binning (primary supervisor) and Professor Poul L. Bjerg (co-supervisor). The work was funded through a PhD scholarship by DTU.

The research was primarily carried out at DTU, but included two external stays at the Institute of Hydraulic Engineering, University of Stuttgart (Sept-Oct 2007, Sept-Dec 2008).

The content of this thesis is based on three scientific journal papers and one conference paper. At the time of writing, two of the journal papers have been published and one is under revision:

I. Troldborg, M., Lemming, G., Binning, P.J., Tuxen, N., Bjerg, P.L. (2008). Risk assessment and prioritisation of contaminated sites on the catchment scale. Journal of Contaminant Hydrology 101(1-4), 14-28.

II. Troldborg, M., Binning, P.J., Nielsen, S., Kjeldsen, P. Christensen, A.G. (2009). Unsaturated zone leaching models for assessing risk to groundwater of contaminated sites. Journal of Contaminant Hydrology 105, 28-37.

III. Troldborg, M., Nowak, W., Tuxen, N., Binning, P.J., Bjerg, P.L., Helmig, R. (2010). Uncertainty evaluation of mass discharge estimates from a contaminated site using a fully Bayesian framework. Water Resources Research (in revision).

IV. Overheu, N., Troldborg, M., Tuxen, N., Flyvbjerg, J., Østergaard, H., Jensen, C.B., Binning, P.J., Bjerg, P.L. (2010). Concept for risk-based prioritisation of point sources. Proceedings of Groundwater Quality 2010. Zurich, Switzerland.

In the thesis, these papers are referred to by author names and Roman numerals.

The papers are not included in this web-version, but can be obtained from the library at Department of Environmental Engineering, DTU, Miljoevej, Building 113, DK-2800 Kgs. Lyngby, Denmark, library@env.dtu.dk.

Additionally, the following reports and publications, related to the topic of the thesis, have been co-authored during the PhD-study, and will also be referred to in the thesis:

Troldborg, M., Nowak, W., Binning, P.J., Bjerg, P.L., Helmig, R. (2010). Uncertainty of mass discharge estimates from contaminated sites using a fully Baysian framework. In: Managing Groundwater and the Environment. IAHS Red Book publication. ModelCARE2009 Wuhan, China.

Christensen, A.G., Binning, P.J., Troldborg, M., Kjeldsen, P., Broholm, M. Upgrading JAGG to version 2.0 - Vertical transport to the first significant aquifer. Published by the Danish EPA, in press. (in Danish).

Jørgensen, P.R., Klint, K.E., Troldborg, M., Binning, P.J. (2008). The JAGG model has been refined to cover risk assessments of aquifers below fractured clay till. VJ Blad. (in Danish)

Tuxen, N., Larsen, L.C., Troldborg, M., Bjerg, P.L., Binning, P.J. (2008). Revised assessment of the existing investigations at Rundforbivej 176. Published by Orbicon A/S for the Capital Region of Denmark (in Danish)

Kgs. Lyngby, May 2010
Mads Troldborg

Acknowledgements

There are a number of people I wish to thank for their help and contribution to this thesis. First of all, I would like to thank my supervisors, Associate Professor Philip J. Binning and Professor Poul L. Bjerg for their superb and competent guidance throughout the entire PhD You are both very inspiring and the main reason I ended up doing a PhD

I owe great thanks to the entire staff at the Institute of Hydraulic Engineering, University of Stuttgart, for two pleasant and very educational stays. I am particularly grateful to Professor Rainer Helmig for his support, cheerful disposition and for funding my stays in Stuttgart, and to Junior-Professor Wolfgang Nowak for introducing me to the world of stochastic modelling and for constantly being available with outstanding guidance and advice.

For great collaboration and co-authorship I would like to thank Nina Tuxen and Gitte Lemming with whom I also had the pleasure of sharing office. Thanks for many good discussions and your numerous valuable comments on my work. Also the co-authors Anders G. Christensen, Peter Kjeldsen, Signe Nielsen, and Niels Døssing Overheu are acknowledged for their contributions to my work. I also wish to thank Carsten Bagge Jensen, John Flyvbjerg and Henrik Østergaard from the Capital Region of Denmark for co-authorship and for providing the information on the cases studied in the thesis.

The Technical University of Denmark and the Otto Mønsted Foundation are gratefully acknowledged for their financial support. The international research school of water resources (FIVA) is greatly appreciated for organising and financing a range of interesting PhD courses.

I would also like to thank my colleagues and friends at DTU, especially the PhD club for cosy events and tasty cakes, Anne Harsting for always being kind and helpful, and Torben Dolin and Julie Camilla Middleton for helping out with graphics and illustrations.

Last, but not least, I would like to thank my family and friends for all their encouragement. I would especially like to express my gratitude to my mum and dad, Niels, Søren and Jennifer for their unconditional love and support.

Abstract

A large number of contaminated sites are threatening groundwater resources worldwide. The expected costs for investigation and clean-up at these sites by far exceed the limited resources available. Regulators are therefore faced with the challenge of prioritising remediation efforts in order to ensure that the sites constituting the greatest risk to groundwater are cleaned up first. Risk assessment is therefore required.

The conventional practice for assessing whether a point source poses a risk to groundwater has been focused on the measurement or prediction of contaminant concentrations at a local scale. If these concentrations do not comply with the contaminant-specific maximum concentration level (generic standards), the point source is considered a risk. The estimation of the concentration levels in groundwater is typically based on contaminant fate and transport modelling. A large number of modelling tools exist for local scale risk assessment. Most of these models are conceptually simple and designed to estimate the contaminant impact from a point source on groundwater using only few inputs and can therefore be applied to many different types of sites.

A literature review has, however, revealed certain limitations of the existing tools for local scale risk assessment of groundwater contamination. It was found that most of the models ignore gas phase transport in the unsaturated zone, although this is known to be a dominant transport mechanism for volatile compounds such as chlorinated solvents and BTEXs. Analytical models accounting for both gas phase and water phase transport as well as sorption and first-order degradation were therefore developed to simulate the contaminant transport through the unsaturated zone. The models were tested on two field sites contaminated with volatile compounds and were found useful for practical risk assessment.

The traditional risk assessment tools are also found less suitable for prioritisation purposes, because they consider the contaminated sites individually and focus only on predicting plume concentrations at a local scale. This is useful for assessing whether a particular contaminated site poses a risk to groundwater, but does not permit prioritisation of sites at larger scales. A modelling tool for risk assessment of contaminated sites on the catchment scale was therefore developed. This screening model evaluates the risk associated with each point source in terms of their ability to contaminate abstracted groundwater at the

water supply in the catchment. It combines site-specific transient mass discharge calculations from all identified sites within the catchment with 3-dimensional catchment-scale contaminant fate and transport modelling. The tool was tested on the groundwater catchment for a water supply located in Denmark and was found to be valuable as a basis for prioritising point sources according to their impact on groundwater quality as well as for identifying the point sources that were most likely to cause the observed contamination at the water supply.

Risk assessments of groundwater contamination are generally subject to data limitations and are therefore prone to large uncertainties. In order to ensure that resources are spent in the most cost-effective manner, it is important that these uncertainties are accounted for. In practice, however, the uncertainty is often not considered, but is handled based on a precautionary principle, where input parameter values are chosen so as to ensure conservative model outputs.

The uncertainties in risk assessment of contaminated sites at local and catchment scale were investigated, particularly focusing on conceptual model uncertainties. An overview of available methods for evaluating the uncertainties in risk assessments was also provided.

At local scale, the uncertainty related to the estimation of contaminant mass discharges from point sources was rigorously evaluated. Such estimates have many useful applications and constitute a key input for the catchment scale risk assessment. A methodology that uses multiple conceptual site models in a Bayesian inverse geostatistical framework was developed for quantifying the uncertainty in mass discharge estimates across multilevel control planes. The method generates an ensemble of flow and transport realisations that all honour the measured data at the control plane from which a mass discharge probability distribution is determined. The method was successfully applied to a TCE contaminated site for which four essentially different conceptual models based on two source zone models and two geological models were formulated. The method also provided a means of testing which of the conceptual site models were most likely to reflect the true site conditions.

At catchment scale, the delineation of the capture zone is critical. The capture zone determines which contaminated sites are potential threats to the water supply as well as the travel times from the individual sites to the water supply. The uncertainty related to the catchment delineation depends on the groundwater model used. It was demonstrated how two different conceptual hydrogeological models could influence the location and extent of a capture zone and hereby affect the catchment scale risk assessment of a contaminated site.

The uncertainties at both local scale and catchment scale hamper the prioritisation of point sources and need to be accounted for to allow a more robust decision-making process. It was demonstrated how an assessment of the uncertainties related to both the mass discharge estimates and the capture zone delineation can be incorporated into the prioritisation using a scoring system. However, the influence of uncertainty on the prioritisation of contaminated sites should be the target for further research, possibly by including economical considerations. Better validation of the risk assessment models at both local scale and catchment scale should also be an issue for future research.

Sammenfatning

Antallet af forurenede lokaliteter, der truer grundvandsressourcerne verden over, er enormt. Sammenlignet med de forventede udgifter til kortlægning og oprensning af de mange lokaliteter er de tilgængelige midler yderst begrænsede. Myndighederne står derfor overfor en udfordring med at få prioriteret oprydningsindsatsen således at de lokaliteter, der udgør den største grundvandsrisiko fjernes først. Risikovurderinger er derfor påkrævet.

Traditionelt har vurderingen af hvorvidt en punktkilde udgør en grundvandsrisiko været fokuseret på målingen eller beregningen af forureningskoncentrationer på lokal skala. Hvis disse koncentrationer overstiger grundvandskvalitetskriteriet vurderes det, at punktkilden udgør en risiko. Estimeringen af koncentrationsniveauerne i grundvandet er typisk baseret på modellering af forureningstransporten. Der findes et stort antal modelværktøjer til risikovurdering på lokal skala. De fleste af disse værktøjer er konceptuelt simple og designet til at estimere forureningsbelastningen fra en punktkilde ud fra kun få input og kan derfor anvendes på mange forskellige typer forurenede grunde.

Et litteraturstudium har imidlertid identificeret visse begrænsninger ved de eksisterende værktøjer til risikovurdering af grundvandsforurening på lokal skala. Det er blevet vist, at de fleste af modellerne ser bort fra gastransport i den umættede zone, til trods for at dette kan være en dominerede transportmekanisme for flygtige stoffer såsom klorerede opløsningsmidler og BTEX'er. Analytiske modeller, der inkluderer transport i både gas- og vandfasen samt sorption og førsteordens nedbrydning, er derfor blevet udviklet til at simulere forureningstransporten gennem umættet zone. Modellerne er blevet testet på to lokaliteter forurenet med flygtige stoffer og er på den baggrund blevet fundet anvendelige til risikovurdering.

De traditionelle risikovurderingsværktøjer er også fundet mindre velegnede til prioriteringsformål, idet de betragter punktkilderne enkeltvist og kun fokuserer på beregning af koncentrationer i forureningsfanen på lokal skala. Dette er nyttigt til at vurdere hvorvidt en given forurenet lokalitet udgør en grundvandsrisiko, men tillader ikke en prioritering af lokaliteter på større skalaer. Et modelværktøj til risikovurdering af forurenede lokaliteter på oplandsskala er derfor blevet udviklet. Dette screeningsværktøj evaluerer risikoen forbundet med hver lokalitet i forhold til deres forureningspåvirkning af det grundvand, der indvindes ved vandforsyningen i oplandet. Værktøjet kombinerer site-specifikke

transiente forureningsfluxbestemmelser fra alle de identificerede lokaliteter indenfor oplandet med 3-dimensionel forureningstransport på oplandsskala. Modellen er blevet testet på grundvandsoplandet til et vandværk placeret i Danmark og er på den baggrund blevet fundet anvendelig til at prioritere punktkilderne ud fra deres forureningsbelastning af grundvandet samt til at identificere hvilke punktkilder, som var de mest sandsynlige årsager til den observerede forurening ved vandværket.

Risikovurderinger af grundvandsforurening er generelt genstand for data begrænsninger og er derfor forbundet med store usikkerheder. For at sikre at de tilgængelige midler bruges på den mest omkostningseffektive måde, er det vigtigt at tage højde for disse usikkerheder. I praksis betragtes usikkerhederne ved risikovurderinger imidlertid ikke, men håndteres typisk ud fra et forsigtigheds-princip, hvor inputværdierne vælges således, at der sikres konservative model resultater.

Usikkerhederne ved risikovurdering af forurenede lokaliteter på lokal og oplandsskala er blevet undersøgt med særligt fokus på de konceptuelle modelusikkerheder. En oversigt over de tilgængelige metoder til evaluering af usikkerhederne i risikovurdering er desuden blevet præsenteret.

Usikkerhederne ved bestemmelse af forureningsfluxe fra punktkilder på lokal skala er blevet omfattende evalueret. Forureningsfluxbestemmelser har mange anvendelsesmuligheder og udgør et væsentligt input til risikovurderingen på oplandsskala. En metode, der benytter flere konceptuelle modeller for en given forurenet lokalitet i et Bayesiansk invers geostatistisk regi, er blevet udviklet til at bestemme usikkerhederne ved forureningsfluxbestemmelser gennem et multi-level kontrolplan. Metoden genererer et ensemble af flow og transportsimuleringer, der alle matcher de målte data i kontrolplanet, hvorudfra en sandsynlighedsfordeling af forureningsfluxen kan bestemmes. Metoden er med succes blevet anvendt på en TCE forurenet lokalitet, hvor fire forskellige konceptuelle modeller baseret på to forureningskildemodeller og to geologiske modeller var blevet opstillet. Metoden gav også mulighed for at teste, hvilken konceptuel model, der bedst repræsenterede de faktiske forhold ved lokaliteten.

På oplandsskala er afgrænsningen af indvindingszone kritisk. Indvindingszonen afgør hvilke forurenede lokaliteter, der potentielt udgør en trussel for vandforsyningen samt hvad transporttiderne fra de individuelle lokaliteter til vandværket er. Usikkerhederne forbundet med afgrænsningen af oplandet afhænger af den anvendte grundvandsmodel. Det er blevet demonstreret, hvordan to forskellige konceptuelle hydrogeologiske modeller influerede på udbredelsen af indvindingszone og derved også påvirkede risikovurderingen af en forurenet lokalitet på oplandsskala.

Usikkerhederne på både lokal og oplandsskala besværliggør prioriteringen af punktkilder og bør håndteres for at sikre en mere robust beslutningstagning. Det er blevet demonstreret hvordan en vurdering af usikkerhederne på både forureningsfluxbestemmelserne og på afgrænsningen af indvindingsoplandet kunne inkorporeres i en prioritering ved hjælp af et scoresystem. Indflydelsen af usikkerheder på prioritering af forurenede lokaliteter bør dog være genstand for yderligere undersøgelser, eventuelt ved at inkludere økonomiske betragtninger. En bedre validering af risikovurderingsmodellerne på både lokal og oplandsskala bør også være et emne for fremtidig forskning.

Table of contents

1 Introduction

1.1 Background and motivation

Contaminated sites are a significant threat to groundwater resources worldwide. The European Environment Agency estimates that there may be as many as 3 million contaminated sites across the EU, of which about 250 000 sites require clean up (EC, 2006; EEA, 2007). The costs for investigation and clean-up of these sites are excessive and compared to the scope of the problem, the available resources for investigating and cleaning up contaminated sites are very limited. Thus, though considerable efforts have already been made, it will still take decades to clean up the legacy of contamination (EEA, 2007). It is therefore crucial that the resources are allocated to the contaminated sites posing the greatest risk. In order to decide which sites should be given the highest priority and to streamline future activities, risk assessment is a very important and useful tool (Cushman et al., 2001; Ferguson et al., 1998).

Contaminated sites are complex environmental problems that require insight into various scientific disciplines such as geology, hydrology, chemistry, microbiology and toxicology. Risk assessments of contaminated sites are useful tools for assembling the concepts and knowledge from these different disciplines in a transparent and scientifically sound way and can thus, if applied sensibly, offer valuable results for decision-making (Ferguson et al., 1998).

1.1.1 Risk assessment at different scales

Various approaches exist for assessing whether a contaminated site constitutes a risk to groundwater (e.g. Spence, 2001; Aziz et al., 2000; Davison and Hall, 2003; Newell et al., 1996). Most of these methods focus on a *local scale* and aim to evaluate if the resulting groundwater concentrations below or downstream of the contaminant source zone are above a certain limit value. If the concentrations do not comply with the regulatory standards the contaminated site is considered a risk. The resulting concentrations can in some case be measured directly, but often need to be calculated from site-specific information regarding released amounts of contaminants, type of contaminant, geology, hydrogeology etc. For the last decade this approach has been common practice in many countries, including Denmark (Bardos et al., 2002).

However, the prioritisation of point sources necessitates that the risk is considered not only on the local scale, but also on larger scales. For an initial prioritisation of contaminated land aquifer vulnerability mapping methods such as DRASTIC (Aller et al., 1987) are widely used. These methods assign scores to different spatially distributed indicators (e.g. top-layer geology, depth to groundwater, recharge and likely types of contaminants spilled), which subsequently are integrated into an overall risk index. Vulnerability mapping helps identifying the areas most susceptible to contamination, but does not account for the degree and extent of contamination at actual sites. Vulnerability mapping can therefore not be used for a more detailed prioritisation of point sources and to identify at which sites remediation should be initiated. Since the motivation for initiating clean-up is often governed by the possible impact on water supply wells, it has been proposed to conduct risk assessments at *catchment scale* (e.g. Einarson and Mackay, 2001; Frind et al., 2006), where the risk of a point source is assessed in terms of its ability to contaminate abstracted water at the supply wells in the catchment. In this context the estimation of contaminant mass discharges from the individual point sources within the catchment has been found valuable (Einarson and Mackay, 2001), because such estimates are dynamic measures of the total contaminant impact.

1.1.2 Risk assessment models

Risk assessments often involve modelling of contaminant fate and transport. The transport and fate of contaminants in the subsurface is, however, complex and depends on a range of physical, chemical and biological factors that may be subject to great variations both spatially and temporally and are affected by both the contaminant properties and the site-specific settings. It is important to account for these various processes in a risk assessment as they have the potential to affect, for example, the mobility and toxicity of the contaminant (Ferguson et al., 1998).

In order to model the complex real-world system several simplifications have to be made. These simplifications should account for the most important site-specific features and dominant processes. Many models for assessing the impact from a contaminated site on groundwater exist and range from simple screening tools to more advanced numerical transport models (ASTM, 1999; Walden, 2005). There is a huge difference in the complexity of these models depending on the specific purpose of the model, the number of processes allowed for, how the processes and site-features are represented mathematically etc.

As risk assessments are often subject to data limitations, they usually rely on analytical models, which have minimal data requirements and thus are applicable even when only basic site data are available. Although analytical models do not allow for the same level of detail and knowledge as numerical models, they are more straightforward to use and are easily applied to many different types of sites. However, it is essential that the risk assessment models do not overly simplify the system in concern, which is very often the case. Not allowing for dominant processes or important site features can lead to substantial under- or overestimations of the risk. For example, neglecting the effect of degradation of biodegradable compounds, the production of metabolites during sequential degradation, preferential flow paths in fractured clay and/or gaseous diffusion in the unsaturated zone for volatile compounds can potentially result in a very misleading risk assessment. Many screening models for risk assessment of groundwater contamination overly simplify the fate and transport in the subsurface. There is still a need for the development of improved risk assessment tools in order to handle the vast number of point sources worldwide. These tools should be able to deal with many different types of contaminants and allow for as many processes and site-specific features as possible, but at the same time not become too data demanding.

1.1.3 Uncertainties in risk assessments

Risk assessments are associated with significant uncertainties. The uncertainties are caused by several factors such as errors in the conceptual model, parameter uncertainty, and errors in applied model algorithm and in data used as input (Beven, 2005; Højberg and Refsgaard, 2005; Walker et al., 2003).

It is important that the uncertainties related to risk assessments of groundwater contamination are taken into consideration to ensure that resources are spent in the most cost-effective manner. An evaluation of the uncertainties determines the reliability of the risk assessment and thus helps clarifying whether more investigations are needed or if action can be initiated. However, uncertainties related to risk assessments of groundwater contamination are often not given much attention. Most of the current risk assessment tools do not include uncertainty considerations at all, and those that do, only take input and/or parameter uncertainties into account. Methodologies for the handling of parameter uncertainty are many, whereas little is known about how to deal with lack of conceptual understanding. This is despite the fact that conceptual uncertainties have been recognised as the most significant sources of error (Konikow and Bredehoeft, 1992; Refsgaard et al., 2006). Thus, there is a need for more systemic research about the influence of uncertainties on risk assessment and for development of methods that can be used for assessing these uncertainties.

1.2 Objectives

The aim of this PhD study has been to investigate methods for risk assessment of groundwater contamination from point sources at both the local scale and the catchment scale and to evaluate the associated uncertainties. The goal is to improve the foundation on which the prioritisation of the remediation efforts is based. Specific objectives have been:

1. On the basis of a review, to identify the limitations of existing tools for risk assessment of groundwater contamination at local scale and to develop new screening models for contaminant transport from point sources (Troldborg et al., I; II).

2. Develop a tool for risk assessment of contaminated sites at catchment scale. The tool will be tested and evaluated on a real groundwater catchment and a ranking of the risk associated with each of the known contaminated sites in the catchment will be carried out (Troldborg et al., I; Overheu et al., IV).

3. To rigorously evaluate and quantify the uncertainties in risk assessment of groundwater contamination from a point source at local scale, specifically focusing on contaminant mass discharge estimates (Troldborg et al., III).

4. To investigate the uncertainties in catchment scale risk assessment and to discuss how these uncertainties can be incorporated into a prioritisation of point sources at catchment scale (Overheu et al., IV).

1.3 Framing of thesis

This PhD thesis focuses on risk assessment of groundwater contamination from point sources (contaminated sites) at both the local scale and the catchment scale. It mainly considers point sources, where contamination has been documented and where data therefore are available. Focus has been placed primarily on organic contaminants such as chlorinated solvents and gasoline compounds, because these compounds are identified as some of the main threats to groundwater in industrial countries due to their mobility and toxicity. Although relevant for these types of contaminations neither mobile free-phase nor multi-component mixtures are considered here. The thesis is centred around solute transport and fate of contaminants in the vadose zone and in groundwater entirely focussing on the impact on groundwater quality. The subsequent exposure of different population subgroups via ingestion etc. is beyond the scope of the thesis. Transport and fate in fractured media are not considered.

1.4 Organisation of thesis

The structure of the thesis is as follows. Chapter 2 gives an overview of the risk assessment terminology adopted in this PhD thesis in order to specify the focus of the thesis and the context in which it should be seen. Local scale risk assessment is described in Chapter 3 and is especially focussed on i) models for contaminant transport in the unsaturated zone, where the findings from Troldborg et al. (II) are elaborated on, and ii) the quantification of the contaminant mass discharge from a site (Troldborg et al., I; III), which is an important input for the catchment scale risk assessment. Catchment scale risk assessment is described in Chapter 4 and elaborates on the findings from Troldborg et al. (I) and Overheu et al. (IV). Chapter 5 presents an overview of the uncertainties involved in risk assessment of point sources and focuses especially on i) the quantification of uncertainties in mass discharge estimates based on the findings in Troldborg et al. (III) and ii) how the uncertainties influence the catchment scale risk assessment based on Overheu et al. (IV). Chapter 6 concludes the outcome of the thesis and discusses topics for further investigations and future research directions.

2 Risk assessment – definitions and terminology

The terminology associated with describing and analyzing risks is relatively new and developing. This has led to ambiguity in the use of terms, both between different risk sciences and between the different parties involved in risk debates (Christensen et al., 2003). The aim of this chapter is therefore to clarify the risk and risk assessment framework used in this PhD thesis and the context in which it should be seen.

2.1 General definitions

Many definitions of risk exist depending on specific applications and situational contexts. The Royal Society provides an overview of the terminology and definitions related to risk management. They define risk as "*the probability that a particular adverse event occurs during a stated period of time, or results from a particular challenge*" (Royal Society, 1992). In general, risk is characterised through a probability of the adverse event occurring (a frequency) and a measure of the associated consequence. Greater consequence and greater likelihood of occurrence lead to a greater overall risk.

Risk assessment refers to the determination of quantitative or qualitative values of risk related to a recognized adverse event. Generally, a risk assessment includes: (1) a hazard identification, where all outcomes potentially leading to harm to humans (injury, property or environmental damage, economic loss etc.) are charted; (2) an estimation of the magnitude of the consequences associated with these outcomes; (3) an assessment of the probability of each of the outcomes; and (4) a risk evaluation, where the results from the first three elements are evaluated and integrated to form a risk picture. Based on the risk picture, comparisons to defined acceptable risk levels can be performed and decisions about how to manage the risk can be undertaken (Royal Society, 1992).

2.2 Risk assessment of contaminated sites

Contaminated sites are a hazard, which may pose a risk if toxic substances reach a given receptor. Risk assessment of contaminated sites deviates from the more classical definition above. A typical risk assessment aims at determining the risk associated with some unwanted future event, for example, what is the chance and consequence of a nuclear power plant melt down or a flooding catastrophe. In risk assessment of contaminated sites the adverse event (the contaminant spill) already did occur, so here it is more ‘just’ a question of a consequence analysis. In principle this should make the risk assessment of contaminated sites easier. However, in practice risk assessment of soil and groundwater contamination is very complex, especially if the need is to predict future exposures (Ferguson et al., 1998). Risk assessment of contaminated sites is a multidisciplinary task that requires insight into geology, hydrology, chemistry, microbiology, toxicology, statistics etc. and involves evaluation of large amount of information and data from various sources.

Risk assessments of contaminated sites are usually based on a source-pathway-receptor concept as illustrated in Fig. 2.1. The pathway is the mechanism by which a contaminant gets from the source to the receptor. A given source can only be a risk if a complete pathway-linkage exists between the source and the receptor. A complete pathway consists of a contaminant release from the source, a transport media (the contaminant of concern can be carried to the receptor contact point in e.g. groundwater, air and/or soil) and an exposure route at the receptor contact point (e.g. the contaminant can reach a human being through ingestion, inhalation or dermal contact). Generally, the following two endpoints are considered in environmental risk assessment: human health and ecological risk. A human health risk assessment evaluates the risks related to human exposures to the contamination, while the ecological risk assessment focuses on protection of flora and/or fauna (US EPA, 2010). In both cases a source characterisation and a pathway evaluation is needed to determine the concentration levels that the given receptor is exposed to.

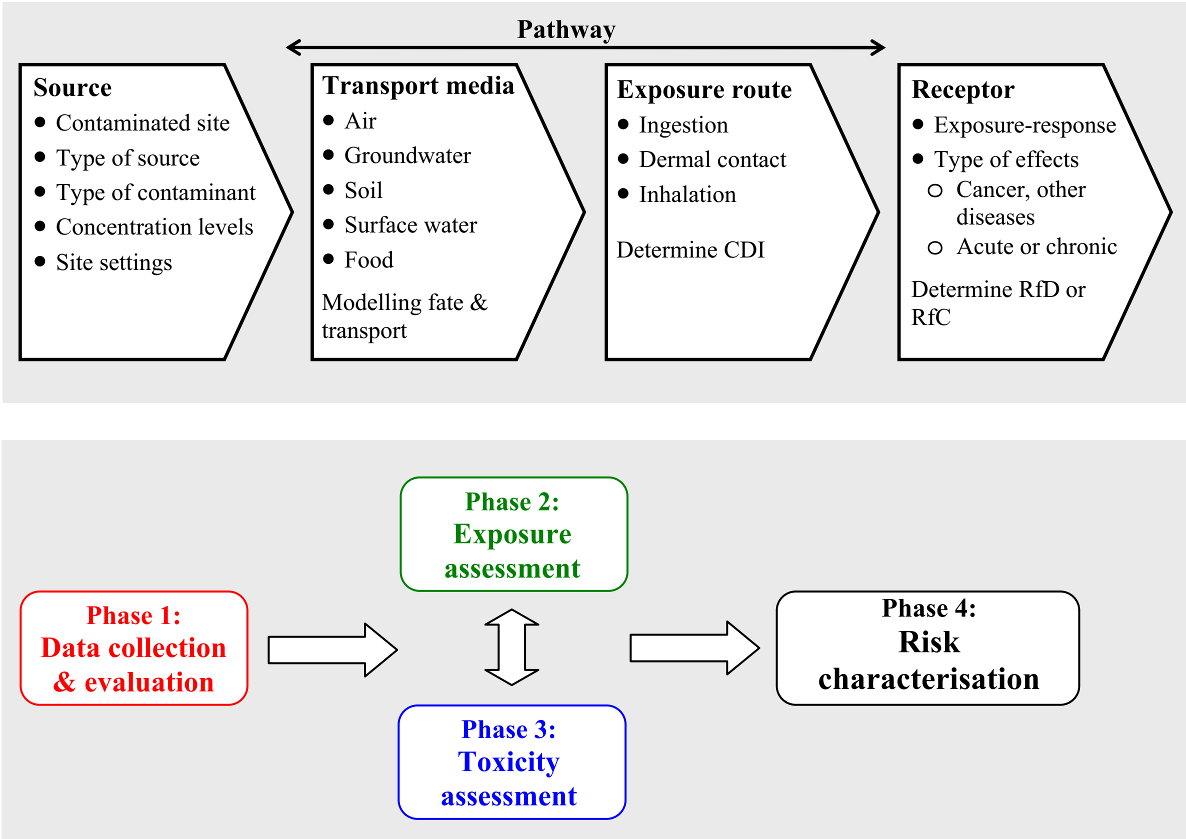


Figure 2.1: Source-pathway-receptor concept of risk assessment. Data collection and evaluation, exposure assessment, toxicity assessment and risk characterisation are fundamental steps in conducting risk assessments of contaminated sites in practice.

In practice, an environmental risk assessment typically involves the following four distinct phases (see Fig. 2.1) (Cushman et al., 2001; Ferguson et al., 1998):

Phase 1 - Data collection and evaluation:
The risk assessment process usually begins with a source characterisation, where data about the contaminant source and information about how the contamination will behave in the future are collected. This data collection and evaluation typically consists of:

- A desktop study that aims at identifying likely contaminants and involves an examination of the historical activities potentially causing contamination together with a study of the soil and aquifer properties affecting spreading (from maps, existing investigations etc.). Based on this, a hypothesis for the source and the possible pathways and receptors is made.

- A field investigation phase that aims at proving the hypothesis and to gather enough information for a complete assessment. This phase involves physical sampling to identify the contaminants of concern, the nature and extent of the contaminant source, the concentration levels, factors controlling transport/fate and the possible exposure pathways.

- A hazard identification, where the inherent properties of the identified contaminants are examined. This includes mapping the contaminants physical-chemical characteristics (e.g. solubility, vapour pressure and Henry's law constant), degradability, bio-accumulative ability and toxicity. This information is used for assembling an environmental profile for the contaminant that describes its possible behaviour and distribution in the environment, and if it has the potential to cause harm following exposure.

The data collection and evaluation should result in the formulation of a conceptual model for the site. The conceptual site model should be updated continually as more data are collected. Once this source characterisation has been carried out and the possible pathways and receptors have been identified, an exposure assessment can be performed.

Phase 2 - Exposure assessment:
Exposure is the condition of a chemical contacting the exterior of a receptor (e.g. a human). Usually, the chemical is contained in a carrier medium (e.g. water, air and food). Exposure assessment is the process of estimating the magnitude, frequency and duration of exposure that may occur due to contact with the contaminated media, both now and in the future. The exposure assessment therefore involves an identification of receptors, an evaluation of exposure pathways and a development of quantitative estimates of exposure for each pathway. The aim is to determine the exposure concentration (i.e. the chemical concentration in the carrier media at the receptor contact point) and the amount of contaminated media taken in by the receptor over time (intake/uptake rate). To quantify the magnitude of the exposure for each pathway, contaminant fate and transport modelling is typically required. The quantified exposures are often expressed as "chronic daily intakes" (CDIs) (Cushman et al., 2001).

Phase 3 - Toxicity assessment:
The toxicity assessment deals with what happens when the contaminant enters the receptor and is the process of estimating exposure-response-relationships. The aim is to determine what the adverse effects are at different exposure levels, when no effects are observed and when responses start to appear. The exposure-response-relationship depends on the specific contaminant, the exposure route (whether the contaminant enters the receptor through e.g. inhalation, ingestion or dermal contact) and the kind of response (tumour, weight loss, death, incidence of disease, etc.). The toxicity can be calculated as a "chronic reference dose" (RfD) or a "chronic reference concentration" (RfC), which both express the maximum daily uptake level of a contaminant that is likely not to result in any adverse effects (Cushman et al., 2001). In soil and groundwater such calculations are often used to define generic standards for the different media and receptors. In practical risk assessments phase 2 and 3 are therefore often partly omitted. This is particularly the case for exposure to contaminated groundwater, where generic standards for groundwater or drinking water substitute the site-specific toxicity assessment and parts of the exposure assessment.

Phase 4 - Risk characterisation:
The risk characterisation summarises the results from the first 3 phases. The results are integrated into quantitative or qualitative expressions of risk, for example as a Hazard Index that relates the CDI to the RfD for all chemicals and exposure routes. Furthermore, the risk characterisation should clearly and consistently present how these risks are assessed and state where assumptions and uncertainties exist. The calculated risks can be compared to acceptance criteria or to other risks to assess whether a risk reduction might be required. The acceptance criteria are often determined politically (e.g. how many additional incidents of cancer are we willing to accept) and are highly affected by the public perception of the risk (Royal Society, 1992).

The above risk assessment description will be used as framework throughout this thesis. However, as the overall focus is risk assessment of contaminated sites based on their impact on groundwater, the toxicity assessment (phase 3) in terms of type of effects, exposure-response relationships etc., has been excluded. How the contaminated groundwater reaches a human being through different exposure routes as part of the exposure assessment (phase 2) is also not considered. Thus, this thesis focuses primarily on the source-pathway part of the risk assessment, and the aim is mainly to use data from site investigations to characterise the source and predict the resulting contaminant impact/concentrations on groundwater at a point of compliance downstream of the source. How the contaminant enters the receptor and what the effects of the exposure are is not considered.

3 Risk assessment at the local scale

The task of managing point sources involves site identification and characterisation, risk assessment, and site remediation. Risk assessments of contaminated sites are traditionally conducted at a local scale, where the aim is to estimate the contaminant impact on various receptors in the vicinity of the source. These receptors can include surface waters, indoor and outdoor air, plants, soil etc., but the focus here is on groundwater.

Figure 3.1 shows a conceptual model for local scale risk assessment of groundwater contamination from a point source located in the unsaturated zone. Two specific source-groundwater pathways are considered:

I) Downward vertical transport of contaminants through the unsaturated zone to the groundwater table.

II) Horizontal transport of contaminants in groundwater

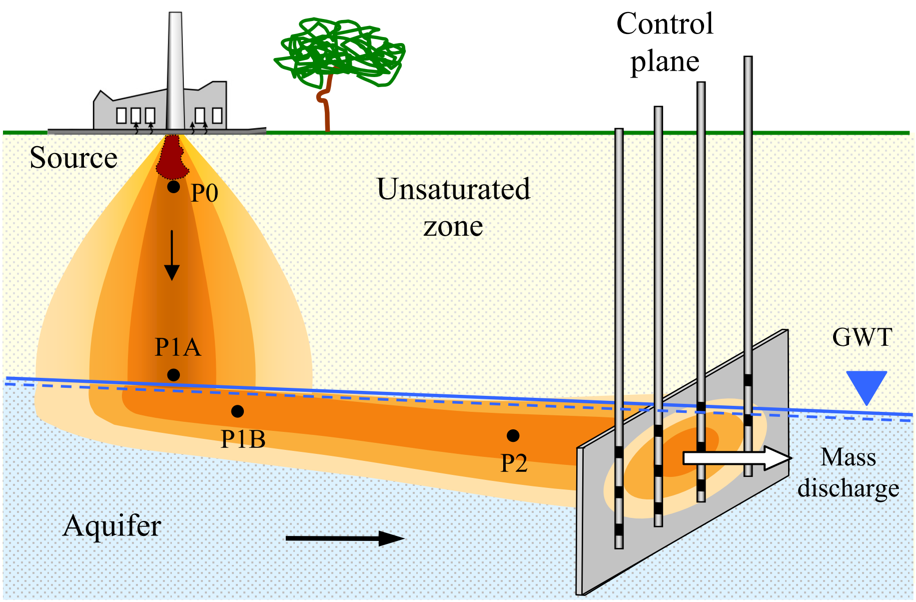


Figure 3.1: General conceptual model for risk assessment of groundwater contamination from a point source at local scale. Different points of compliance (P1A, P1B and P2) are indicated representing common outputs of a risk assessment. An estimation of the mass discharge through a (compliance) control plane is also a commonly applied measure of risk. Note that the location of P2 and the control plane are only indicative. The location of P2 varies among specific risk assessment models, while the control plane position usually is site-specifically determined.

These pathways involve transport and fate in water, air and soil, and also free phase transport for specific types of contaminants. The pathways included depend on the location of the source and in some cases the vertical transport pathway in the unsaturated zone might be excluded.

The output of a local scale risk assessment usually consists of the prediction of contaminant concentration levels in groundwater at a point of compliance (see Fig. 3.1 and the section 3.1). However, recent literature has questioned whether the use of concentrations should comprise the sole measure of risk (Einarson and Mackay, 2001; Nichols, 2004; US EPA, 2003) and there is now a growing consensus among regulatory agencies and technical groups to use estimates of mass discharge as supplemental measure in risk assessment and remediation design at contaminated sites (Basu et al., 2006).

The exposure routes typically considered for risk assessment of groundwater contamination are ingestion of water through drinking or via food and plants irrigated with contaminated water, dermal contact (e.g. showering) and inhalation. Table 3.1 summarises the source-pathway-receptor concept for local scale risk assessment.

Table 3.1: Summary of source-pathway-receptor concept at local scale

Source	**Pathway**	**Receptor/output**
Point source • Documented contamination • Data exist	Fate and transport • Air (only in vadose zone) • Water • Soil • Separate-phase (residual or mobile)	Groundwater • Concentration in point of compliance • Mass discharge

3.1 Generic standards

The conventional practice for assessing whether a point source poses a risk to groundwater has been centred on the measurement or prediction of contaminant concentrations throughout the site. These concentrations should then comply with generic standards that usually are expressed as a contaminant-specific maximum concentration level (MCL) for the source or for the media that the receptor is exposed to. If the concentrations do not comply with these standards, the point source is said to be a risk. Often the concentration levels are estimated at points, so-called points of compliance. Although there are no universal point of compliance locations, the following locations are often considered as indicated on Figure 3.1 (e.g. in ASTM, 1999; Danish EPA, 2002; 1998; Davison and Hall, 2003):

- P0: in the source zone
- P1A: at the groundwater table immediately below the source zone, i.e. what are the maximum concentrations reaching the groundwater.
- P1B: in groundwater immediately below the source zone
- P2: in groundwater at a specified distance downstream of the source.

The point of compliance considered and their exact location vary from country to country. For example, Denmark operates with a P2-type of compliance point that is located at a distance corresponding to one year of groundwater flow from the source zone, though maximum 100 m. At this theoretical calculation point, the groundwater quality criteria must be met (Danish EPA, 2002; 1998).

Generic standards are often based on a reverse risk assessment approach (see exposure and toxicity assessment in section 2.2), where the acceptable risk at the receptor is back-calculated to the corresponding maximum allowable contaminant concentrations at the source (Cushman et al., 2001). Sometimes the generic standards are based entirely on a political decision, e.g. as in Denmark, where it was decided to set the groundwater criteria for pesticides to 0.1 μg/l, which was the analytic detection limit in 1980, and is equal to the EU limit value for pesticides in drinking water (i.e. after treatment) (Helweg, 2000).

Several countries base their risk assessment practice on generic standards (Bardos et al., 2002; Ferguson et al., 1998). The use of generic standards is a transparent and easy approach that helps streamlining the entire risk assessment process, since the standards can be applied to multiple sites. However, generic standards are generally considered very conservative and do not account for unique site-specific properties that might have a significant influence on the risk. Initiating clean-up based only on exceeded generic standards can therefore end up being very costly (Ferguson et al., 1998). In practice, this means that generic standards are often used as a preliminary site assessment and used for determining where and if more detailed investigations are needed.

3.2. Risk assessment at different knowledge levels

Although risk assessment practices and legislations on contaminated land vary among countries, a tiered procedure for the management of contaminated soil and groundwater is usually employed (Bardos et al., 2002). The intention of the tiered approach is to let the analysis progressively become more complex as more data are collected and hereby reduce the uncertainties as well as the need for conservative assumptions. A tiered risk assessment is thus tailored to the knowledge level and site-specific conditions (Pollard et al., 2002).

Table 3.2 presents a tiered approach for risk assessment of contaminated sites, adapted from existing approaches (e.g. ANPA, 2002; ASTM, 1999; Davison and Hall, 2003; EA, 2004; Pollard et al., 2002). To avoid confusion and to distinguish it from the previously presented approaches the tiers are here termed levels.

Table 3.2: Risk assessment at different knowledge levels

Knowledge	Level	Approach	Tools/methods	Uncertainty
Low	0	Screening (suspicion)	GIS, databases, maps. Desktop mapping of industries and sites, expected compounds, aquifer vulnerability	High
↓	1	Generic standards.	Field investigations. Databases and simple screening models	↓
↓	2	Site-specific fate and transport modelling	More field investigations. Analytical models	↓
High	3	Detailed site-specific fate and transport modelling	Detailed field investigations. Numerical models	Lower

3.2.1. Level 0

The initial step consists of a site being mapped due to suspected contamination. This desktop mapping is typically based on whether former or current activities at the site could have resulted in a potential contamination. Although this step does not assess any risks directly, a semi-quantitative screening of the risks can be carried out. This type of screening often relies on index methods for groundwater vulnerability mapping, where different indicators (e.g. soil texture, geology, depth to groundwater table, recharge, site history, likely contaminants and whether the site is located in an area of special water or land-use interests) are given scores and weights, and subsequently integrated, typically by use of GIS, into an overall vulnerability index. Aquifer vulnerability mappings are usually employed at larger scales and can help identifying areas most susceptible to contamination and hereby elucidate where site investigations should be targeted.

The DRASTIC system (Aller et al., 1987) is one of the most widely used index methods for aquifer vulnerability mapping. DRASTIC considers seven geological and hydrogeological factors, but is independent of the nature of contaminant, and thus is categorised as an intrinsic vulnerability method (Frind et al., 2006). Different modifications of the DRASTIC method have been proposed in the literature (e.g. Babiker et al., 2005; Bojorquez-Tapia et al., 2009), many of which have aimed to provide specific vulnerability maps, where contaminant use and behaviour are also accounted for (e.g. Nobre et al., 2007; Secunda et al., 1998; Tait et al., 2004b). In Denmark the system GISP (GIS-based Prioritisation) has been developed for the initial screening and prioritisation of sites and is a modification of DRASTIC (Danish Regions, 2007). GISP combines maps of the intrinsic vulnerability (based on factors such as recharge, thickness of protective clay layer, aquifer and water type, depth to aquifer, and distance to water supply) and administrative vulnerability (considers whether a site is located in an area of special drinking water interests and/or within groundwater catchment zones) with an industry-compound-index (considers type of activities, likely or documented presence of contaminants, and contaminant mobility, toxicity and degradability).

Groundwater vulnerability methods such as DRASTIC have received much criticism, because they usually do not account for actual measurements of contaminant concentrations. Several studies have found poor correlation between vulnerability maps and field measurements of contaminants (Rupert, 2001). To overcome this problem Worrall and Kolpin (2003) suggest calculating aquifer vulnerability based on concentration data from monitoring wells, while Rupert (2001) calibrates modified DRASTIC vulnerability maps with actual groundwater quality data. However, in order to prioritise the remediation efforts at point sources more site-specific information must be included.

3.2.2. Level 1

In the next step some initial field investigations are carried out to document whether and to what extent contamination is present. At this stage, the risk assessment simply consists of a comparison of the measured contaminant concentrations with generic soil and groundwater criteria. If these criteria are exceeded the site is considered a risk. A Level 1 assessment does not account for the effect of dilution or attenuation of the contamination and is therefore considered to be the most conservative approach.

3.2.3. Level 2

A number of processes and reactions influence the distribution, fate and transport of the contamination in the environment. This behaviour depends not only on the physical and chemical properties of the contaminant, but also very much on a range of site-specific conditions. It is generally recognised that these site-specific characteristics are important and should be accounted for in risk assessments. This is usually done via a forward approach, where site-specific data from the source and pathway modelling is used to determine if the resulting risk at the receptor point is acceptable or not (Cushman et al., 2001).

A level 2 risk assessment involves fate and transport modelling to account for these site specific conditions. Through fate and transport modelling the aim is to improve our understanding of how contaminants are affected by the physical, biological and chemical processes that occur within and in the vicinity of a contaminated site. Several modelling tools exit for assessing the impact from a contaminated site on groundwater (see section 3.3). The models used at this level are typically simple analytical tools, which rely on relatively few inputs and therefore can be applied at early stages.

The output of the modelling is in far the most cases a prediction of the concentration levels in groundwater. By comparing the predicted concentrations to groundwater criteria it can be evaluated if a contaminant source poses a risk to the groundwater or will be a risk in the future (Danish EPA, 2002).

3.2.4. Level 3

The aim and output of a level 3 risk assessment is basically the same as for level 2. A level 3 risk assessment allows for the incorporation of more site-specific knowledge and requires that more data are collected at site. Level 3 risk assessments are based on more sophisticated (typically numerical) models, which can account for the more complex nature at the site such as heterogeneity, time-dependent transport, complex transformation reactions etc. To justify the use of a numerical model in the risk assessment, the results from the model typically has to be verified through some calibration and validation procedure.

3.3 Mass discharge

Recent literature suggests using estimates of the mass discharge[1] (mass/time) as a supplement to predicted concentrations, when assessing the impact that a point source has on groundwater (e.g. Einarson and Mackay, 2001; Feenstra et al.,

[1] Note that there is some debate about the term mass discharge (Nichols, 2004). Among the terms used in the international literature for this quantity are mass discharge (Guilbeault et al., 2005; Einarson & Mackay, 2001), mass flux, contaminant flux (Arey & Gschwend, 2005; Soga et al., 2004; Hatfield et al., 2004; Bockelmann et al., 2003; Kao & Wang, 2001; King et al., 1999) and source strength (Falta et al., 2005).

1996; Nichols, 2004; US EPA, 2003). The mass discharge (MD) is defined as the contaminant mass per unit time that migrates across a hypothetical control plane located downstream of the source and perpendicular to the mean groundwater flow (cf. Fig. 3.1). It is calculated by integrating the contaminant concentration and the groundwater flow over the area A of the control plane:

$$MD = \int_A \mathbf{n_A q C} dA \tag{3-1}$$

where $\mathbf{n_A}$ is a unit vector normal to the control plane, and $\mathbf{q}$ and $\mathbf{C}$ are the darcy flux field and concentration field at the control plane, respectively.

The mass discharge is a dynamic measure of the total contaminant impact from a given source and has found many useful applications in the literature. Mass discharge estimates have for example been found valuable for the assessment of natural attenuation rates in plumes (e.g. Basu et al., 2006; Bockelmann et al., 2001; 2003; Kao and Wang, 2001; King et al., 1999) and for evaluating the potential impact on down-gradient receptors (e.g. Troldborg et al. I; Einarson and Mackay, 2001; Feenstra et al., 1996; Kalbus et al., 2007). The coupling of estimates of the mass discharge and the source mass has furthermore gained considerably research attention over the past decade, especially for DNAPL sources (e.g. Basu et al., 2008; Christ et al., 2006; Falta et al., 2005b; Park and Parker, 2005; Parker and Park, 2004; Zhu and Sykes, 2004). This coupling is essentially a mass balance approach and is found valuable for estimating the source longevity and long-term impact on groundwater, assessing remediation timeframes and evaluating the benefits of source zone remediation (e.g. Falta, 2008; Jawitz et al., 2005; Soga et al., 2004).

Different methods for determining the mass discharge in the field exist as illustrated in Fig. 3.2. These have the common feature that the mass discharge is determined through a control plane of wells established downstream of the source and perpendicular to the overall water flow. In order to estimate the total mass discharge it is important that the wells are located in such way that the plume is fully covered. The most commonly applied method is the multilevel sampling approach, where the mass discharge is estimated from measurements of contaminant concentration and flow rate at a number of points in a multi-level sampling network (e.g. Troldborg et al. (III); Kao and Wang, 2001; King et al., 1999; Soga et al., 2004; Tuxen et al., 2003). Other notable approaches for mass discharge estimation are: the passive flux meter that aims at measuring the mass flux at each monitoring point directly using a permeable sorptive unit (Annable et al., 2005; De Jonge and Rothenberg, 2005; Hatfield et al., 2004), and the integral pumping test that determines the mass discharge from an inversion of concentration-series measured over time in the water pumped from pumping wells installed along the control plane (e.g. Bauer et al., 2004; Bockelmann et al., 2001; 2003; Herold et al., 2009; Jarsjö et al., 2005).

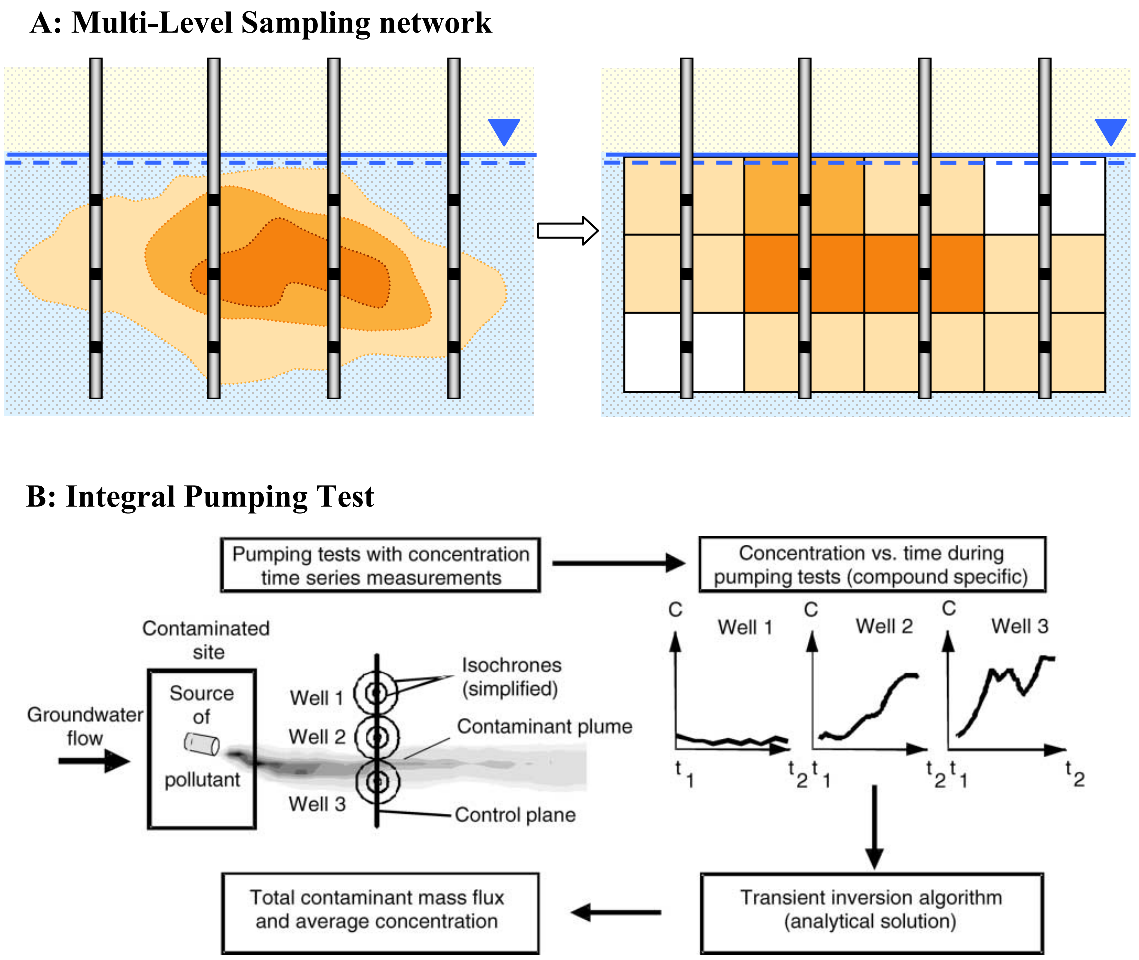


Figure 3.2:. Methods for quantifying mass discharge in the field. A: multilevel sampling network. B: integral pumping test (from Bockelmann et al., 2001, with permission).

The multi-level sampling and the integral pumping test approach provide a snapshot of the mass discharging through the control plane, while the passive flux meter approach provides a time-integrated mass discharge estimate and thus is less prone to temporal concentration variations. The methods have different advantages and drawbacks; which approach is the best depends on the site conditions, the project objectives and budgetary limitations (Suthersan et al., 2010). The different approaches have been compared in different studies and are generally found to yield comparable estimates of the mass discharge (e.g. Brooks et al., 2008; Bockelmann et al., 2003; Kubert and Finkel, 2006; Tuxen et al., 2006; Beland-Pelletier et al., submitted).

Moreover, a range of model tools have been developed for estimating the mass discharge. Generally, these tools calculate the mass discharge from information about water flow, source area, source mass and concentration levels. Some of these models will be examined in section 3.3.1.

A limitation of using mass discharge in the assessment of point sources is that these estimates can be prone to rather large uncertainties as they integrate uncertain distributions of both concentration and water flow (Nichols, 2004). A flux-based risk assessment generally requires a well characterised site with many data to obtain a reliable mass discharge estimate and so mass discharge estimates are more likely to be employed at later stages in a risk assessment. Furthermore, while a concentration-based risk assessment is easily related to limit values and thus can support decision-making this is presently not as straightforward for a flux-based risk assessment. Flux-based risk assessments are therefore less easy for the public to understand.

3.4 Risk assessment tools

Where receptors are not directly exposed to contaminants, the risk assessment will have to be based on a prediction of the risk. This relies on an understanding of how risks might occur and often involves the use of modelling. Models are powerful tools for integrating the various elements of a risk assessment such as site characterisation, transport and fate of contaminants and exposure to groundwater receptors. A large number of risk assessment and decision support tools exist for simulating and evaluating the impact from a contaminated site on groundwater. The complexity of these models range from simple screening tools to more advanced numerical transport models (ASTM, 1999; Walden, 2005). The complexity usually depends on the purpose of the model is and the stage in risk assessment it is developed for.

Regardless of model complexity, the real-world system can only be represented approximately by a model. In order to do modelling and predictions it is necessary to simplify the system in question. The simplifications are necessary for describing complex phenomena such as heterogeneous geology, hydrogeology, contaminant source distribution and spreading and transformation processes. The simplification is done through conceptualization, where the most important site-specific features and dominant processes are identified. Every model has its foundation in a conceptual model. The formulation of conceptual models for the contaminated sites is a key issue of risk assessments, and supports the identification and assessment of pollutant linkages (EA, 2004). The conceptual model can be defined as a hypothesis for how a system or process operates and is based on the subjective judgment by the analyst. The conceptual model can be expressed quantitatively as a mathematical model (analytical or numerical) through which the appropriateness of the conceptual model can be tested by comparing model simulations to field observations (Bjerg et al., 2009; Bredehoeft, 2005; Konikow and Bredehoeft, 1992).

Table 3.3 presents a selection of models considered especially useful for Level 2 risk assessments of groundwater contamination at local scale. The local scale models developed in Troldborg et al. (I) and (II) have also been included in the table, while numerical models deliberately have been excluded. The table gives an overview of the features included in these widely used models. These models all use site-specific information regarding released amounts of contaminant, geology, hydrogeology etc. to calculate the resulting concentrations in groundwater. Because the main focus is on concentration in a migrating plume or at some downstream receptor point, the risk is very dependent on processes like advection, dispersion, degradation, sorption and equilibration reactions. However, most of the tools also aim at quantifying the mass discharge over time from the source.

Table 3.3: Models for local scale risk assessment of groundwater contamination

Models for assessing the contaminant impact on groundwater at local scale	i) JAGG	ii) BIOCHLOR BIOSCREEN	iii) RISC4	iv) ConSim	v) BIOBALANCE	vi) Rome	Troldborg et al. ,(I)	Troldborg et al., (II)
General								
Aim/output: Concentration in point (CP) Natural attenuation (NA) Mass reduction (MR) Mass discharge (MD) Effect of remediation (ER)	CP	CP NA MR MD	CP NA MR MD	CP NA MR MD	CP NA MR MD ER	CP NA	MR MD	CP NA
Stationary (S) Transient (T)	S	S+T	S+T	S+T	S+T	S	S+T	S+T
Data base	X		X	X		X		
Built-in uncertainty analysis			X	X				
Source								
Number of source modules	2	1	3	2	2	4	2	2
Source strength function: Continuous (C), Decaying (D), Pulse (P), User specified (U)	C	C D	C D P	C D U	C D	C	C D	C
Residual NAPL phase			X	X	X	(X)	X	
Unsaturated zone								
Infiltration	X		X	X	X	X	X	X
Diffusion in gas								3D
Dispersion in water			1D	1D				3D
Degradation			X	X			X	X
Sorption			X	X		X	X	X
Fracture				X				
Saturated zone								
Advection (1D)	X	X	X	X	X	X	X	
Hydrodynamic dispersion	1D	3D	3D	2D	3D	3D		
Degradation: First order (F) Sequential (S) Competition (C) Degradation zones (Z)	F	F S C Z	F	F	F C	F	F S Z	
Sorption	X	X	X	X	X	X	X	
Mixing depth	0.25 m	User input	Calc	Calc	User input	Calc	User input	

i) JAGG is the risk assessment tool developed by the Danish EPA (Danish EPA, 2002)

ii) BIOSCREEN (Newell et al., 1996) and BIOCHLOR (Aziz et al., 2000) developed by the US EPA

iii) RISC4 is a commercial risk assessment model (Spence, 2001)

iv) ConSim is a commercial model developed for the UK Environment Agency (Davison and Hall, 2003)

v) BioBalance is a freeware from Groundwater Services Inc. (Kamath et al., 2006)

vi) ROME is developed by the Italian National Agency for Protection of the Environment (ANPA, 2002)

3.4.1 Source models

The models presented in Table 3.3 differ in how the source zone is or can be represented. Some of the models allow the selection of different source modules. For example, RISC4 (Spence, 2001) and ConSim (Davison and Hall, 2003) are capable of simulating transport of contaminants from a point source located in either the unsaturated zone or the saturated zone, while BIOSCREEN (Newell et al., 1996) and BIOCHLOR (Aziz et al., 2000) only consider a source in the saturated zone.

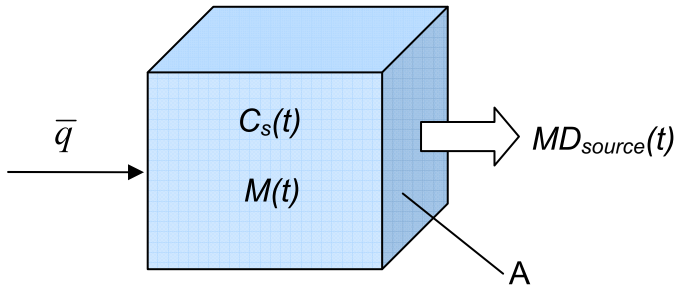


Figure 3.3: Simple conceptual source model

In many cases the source zone is conceptualised as a box (Fig. 3.3), where the complex contaminant source distribution is described by up-scaled or effective parameters. Analytical expressions for describing the leaching from the source zone with time (source strength functions) can then be derived. The tools in Table 3.3 include different source strength functions. For example, RISC4 allows the impact from an instantaneous pulse release of contaminants to be simulated. All the models can simulate the effect of having a continuous source zone concentration, C_0, resulting in a constant mass discharge, MD_{source}, leaving the source with time:

$$MD_{source} = A \cdot \overline{q} \cdot C_0 \tag{3-2}$$

where A is the source area perpendicular to the overall water flow direction and $\overline{q}$ is the effective Darcy flow rate through the source zone. An implication of applying this simple leaching description in a risk assessment is that the output eventually will become stationary (assuming steady flow conditions as well). For point of compliance-based risk assessments this means that a stakeholder often only needs to evaluate a single value (the steady-state concentration) in order to assess the risk, which can appear attractive from a practical point of view. The limitation of using Eq. (3-2) as a source term in a risk assessment is, however, that it assumes an infinite source mass and thus does not allow for an estimation of the impact duration, which generally is considered a key output in an exposure assessment (c.f. Chapter 2).

Most of the tools in Table 3.3 are also capable of simulating source decay as a result of the contaminant mass leaching from the source. The decrease in source mass, *M*, as a function of time is usually described as:

$$\frac{dM}{dt} = -A \cdot \overline{q} \cdot C_s(t) \tag{3-3}$$

where $C_s(t)$ is the effective transient concentration leaving the source zone. Some authors include an additional term to Eq. (3-3) to account for source decay due to for example degradation (e.g. Falta, 2008; Troldborg et al., I). Degradation in the source zone is often expected to be much smaller than the leaching out of the source (Eq. 3-3), but could be significant when investigating the long-term leaching (Falta et al., 2005b).

Different analytical expressions have been proposed to describe how the outflow concentration relates to the source mass and the water flow through the source. Notable analytical expressions are presented in the Table 3.4. The Power Law Model is a widely used expression for relating the source strength to the source mass (e.g. Zhu and Sykes, 2004; Basu et al., 2008) and is given by:

$$\frac{C_s(t)}{f_c S} = \left(\frac{M(t)}{M_0}\right)^{\Gamma} \tag{3-4}$$

where S is the aqueous solubility of the compound, f_c is the ratio between the initial effective concentration, $C_s(t=0)$ and the aqueous solubility, M_0 is the initial source mass and Γ is an empirical fitting parameter that accounts for the variability in both the source zone distribution and the flow field. The relationship between source concentration and mass is non-linear for all values of Γ, except 0 and 1. Generally it is found that $\Gamma > 1$ for low-permeability zones, while $\Gamma < 1$ for high permeability zones with good contact between advecting water and the contamination (Falta et al., 2005a; Falta et al., 2005b). However, many field cases have indicated that a Γ value of 1 seems appropriate (e.g. McGuire et al., 2006; Newell et al., 2006).

By combining Eq. (3-3) and (3-4), Falta et al. (2005a) derive closed-form analytical solutions for $C_s(t)$, $M(t)$ and the mass discharge $MD_{source}(t)$ over time for different values of Γ. To describe the dissolution from a source, most of the tools presented in Table 3.3 employ Eq. (3-4) with Γ = 1 to indicate a linear equilibration between the mass and concentration. An exponentially decaying source mass and mass discharge is then obtained:

$$MD_{source}(t) = A \cdot \overline{q} \cdot S \cdot f_c \exp(-k_s t) \tag{3-5}$$

with k_s being the first-order source decay given by:

$$k_s = \frac{q \cdot A \cdot f_c \cdot S}{M_0} = \frac{q \cdot A \cdot C_0}{M_0} \tag{3-6}$$

This approach for describing the leaching from a source zone was also applied in Troldborg et al. (I). However, instead of using a single box to represent the source zone, they suggested a modular leaching model consisting of coupled reactors each representing different compartments of the source. The idea is that the reactors are assembled to represent the source zone as well as possible, depending on the specific site and the data availability. When more data are available, a more detailed model can be justified. The leaching model by Troldborg et al. (I) was further developed to account for presence of a residual NAPL phase in the source zone. The leaching from an area containing residual phase was modelled by setting Γ = 0 leading to a constant mass discharge leaving the source. The mass discharge was assumed to remain constant for as long as residual phase is present in the source after which Γ is again equal to 1 and the mass discharge decreases exponentially.

BioBalance includes a similar leaching model, where the mass discharge is assumed constant until 50% of the source mass has been depleted (Kamath et al., 2006). Arey & Gschwend (2005) present a source model that describes the leaching of contaminants to groundwater from a LNAPL pool on top of the groundwater table, which is based on Eq. (3-5), but where the transverse area, *A*, is calculated based on dispersion-induced vertical mixing.

Parker & Park (2004) present a leaching model based on the estimation of an effective Damkohler number, which represents the ratio between hydraulic residence time and the mass transfer reaction time. Their Damkohler Model is given in Table 3.4 (Basu et al., 2008; Parker and Park, 2004). The Damkohler number ($=K_{eff}L/\bar{q}$) depends on the effective mass transfer coefficient k_{eff}, which again depends on the empirical parameters k_0, β_1 and β_2. β_1 expresses the rate-limited dissolution depending on the contact time between the contaminant phase and the advecting water, while β_2 describes the mass depletion and depends on the flow field, the source architecture and the correlation between the two (Basu et al., 2008; Parker and Park, 2004).

In the Equilibrium Streamtube Model the source zone is conceptualised as a collection of non-interacting streamtubes, where the heterogeneity of the flow field and the source (DNAPL) distribution within the streamtubes is described through a reactive travel time parameter, τ (Jawitz et al., 2005; Basu et al., 2008). τ represents the time at which a given streamtube is depleted of contaminant mass for a specific set of dissolution conditions and contaminant properties (Basu et al., 2008). For the Equilibrium Streamtube Model expression presented in Table 3.4 it is assumed that τ follows a log-normal distribution, where the mean ($\mu_{\ln\tau}$) and standard deviation ($\sigma_{\ln\tau}$) of $\ln\tau$ are considered to be fitting variables.

Table 3.4: Selected source zone leaching models

Source model	**Expression**	**Reference**	**Application**
Damkohler Model	$\frac{C_s(t)}{C_0} = 1 - \exp\left(-\frac{k_{eff}L}{\bar{q}}\right)$ where $k_{eff} = k_0\left(\frac{\bar{q}}{\bar{K}_s}\right)^{\beta_1}\left(\frac{M(t)}{M_0}\right)^{\beta_2}$	Parker & Park (2004) Basu et al. (2008)	Developed mainly for DNAPL dissolution
Power Law Model	$\frac{C_s(t)}{f_c S} = \left(\frac{M(t)}{M_0}\right)^{\Gamma}$	Falta et al. (2005b) Zhu & Sykes (2004) Troldborg et al. (I) Fraser et al. (2008) Arey & Gschwend (2005)	Mainly used for dissolution of DNAPL, but also LNAPL and creosote
Equilibrium Streamtube Model	$\frac{C_s(t)}{f_c S} = \frac{1}{2} - \frac{1}{2}erf\left(\frac{\ln t - \mu_{\ln\tau}}{\sigma_{\ln\tau}\sqrt{2}}\right)$	Jawitz et al. (2003; 2005) Basu et al. (2008)	Developed mainly for DNAPL dissolution

C_s: average solute concentration leaving source zone. C_0: initial solute source zone concentration.
f_c: fraction between initial source zone concentration and aqueous solubility.
K_{eff}: effective mass transfer coefficient. $\bar{K}_s$: effective saturated hydraulic conductivity of the source.
M: contaminant source mass. M_0: Initial contaminant source mass. S: aqueous solubility.
L: source zone length in water flow direction. $\bar{q}$: average Darcy flow through source zone.
Γ, k_0, β_1, β_2, $\mu_{\ln\tau}$ and $\sigma_{\ln\tau}$ are empirical fitting parameters

In order to evaluate the ability of the different source models to simulate leaching from sources (especially containing DNAPL), several studies have tested them on synthetic cases based on numerical multi-phase modelling (e.g. Christ et al., 2006; Basu et al., 2008; Parker and Park, 2004), while fewer experimental applications are available especially in the field (Fraser et al., 2008; Fure et al., 2006; King et al., 1999).

Eq. (3-3) is more correct from physical point of view and can provide the user with an estimate of source longevity and impact duration. However, the utility of the upscaled source models for simulating leaching under various conditions depends on whether the empirical parameters (e.g. Γ,τ, β_1 and β_2) can be properly estimated. These empirical parameters can have a dramatic influence on the source behaviour over time and are generally not easily determined. Christ et al. (2006) demonstrate that the lumped empirical parameter values are site specific and cannot easily be transferred from one site to another. They suggest an upscaled model, which is based on parameters that can be measured in the field (the ganglia-to-pool ratio and the initial flux-averaged concentration leaving the source) to determine the transient source behaviour. At the moment, considerable research is focussed on the determination of appropriate parameter values for these models under different site-conditions (e.g. Basu et al., 2008; DiFilippo and Brusseau, 2008; Falta et al., 2005a; Falta, 2008). The analytical leaching models can, however, still help investigating the effect of source and flow heterogeneity in a simple way by treating the empirical parameters as random variables.

Another critical issue related to the source zone models is that the initial source mass has to be estimated, which in most practical cases is very difficult. The implication of using the decaying source modules is also that the output of the risk assessment is transient. Although a transient output provides a better foundation for decision-making, it might also in some cases be less transparent, for example if the impact from different sources is to be compared, e.g. a high mass discharge in a short period versus a lower mass discharge in a long period.

3.4.2 Unsaturated zone

Most point sources originate from contaminant releases at or near the land surface. In order for contaminants to reach an underlying aquifer they must pass vertically through the unsaturated zone. During the transport through the unsaturated zone the contaminants are subject to various attenuation processes, which often significantly influence the risk that a point source constitutes to groundwater. It is therefore critical to account for these attenuation processes in the unsaturated zone when assessing the risk of groundwater contamination from point sources. However, the transport in the unsaturated zone is rather complex as the contaminants can be transported in two phases (gas and water) that are coupled to each other and also vary both spatially and temporally.

As indicated by Table 3.3, the risk assessment tools describe the transport through the unsaturated zone in a very simplified manner that completely ignores the effect of gas phase transport. Generally, most risk assessment tools are found only to consider solute transport in infiltrating water (Karapanagioti et al., 2003). An implication of this is that point sources located under paved areas, where recharge is neglectable, will not pose a threat to groundwater. Many studies have, however, shown that transport in the gaseous phase is dominant, especially for volatile compounds such as BTEX and chlorinated solvents. For example, gas phase diffusive transport has in many cases shown to contribute significantly to the migration of contaminants to the groundwater table (Baehr et al., 1999; Dakhel et al., 2003; Pasteris et al., 2002) and to the spreading of contamination over a larger area resulting in lower concentrations reaching the groundwater (e.g. Christophersen et al., 2005; Conant et al., 1996). Gas phase advection due to gas density gradients, barometric pressure variations, fluctuating groundwater table and temperature changes has also shown to be an important transport mechanism for volatile organic compounds (e.g. Auer et al., 1996; Mendoza and Frind, 1990; Parker, 2003; Falta et al., 1989). Furthermore, for a wide range of oil components aerobic microbial degradation is identified as a significant attenuation process in the unsaturated zone (DeVaull et al., 2002; DeVaull et al., 2002; Hohener et al., 2006; DeVaull et al., 2002; Hohener et al., 2006; Lahvis et al., 1999), and has the potential to greatly reduce the contaminant impact on groundwater.

Generally, a risk assessment model should incorporate the most important and dominant processes. Though many risk assessment models and analytical solutions exist for simulating contaminant transport in the unsaturated zone (e.g. ASTM, 1999; Jury et al., 1983; Ravi and Johnson, 1997; Shan and Stephens, 1995; Unlu et al., 1992; Connell, 2002), the majority of these do not account for both the combined gas and water phase transport and/or biodegradation and usually describe the vertical transport as one-dimensional. This lack was identified by Troldborg et al. (II), where a general approach for deriving water and gas phase analytical solutions describing the downward vertical contaminant transport through the unsaturated zone from a surface-near source to an underlying aquifer was developed. The conceptual model for the downward vertical fate and transport through the unsaturated zone is shown in Fig. 3.4.

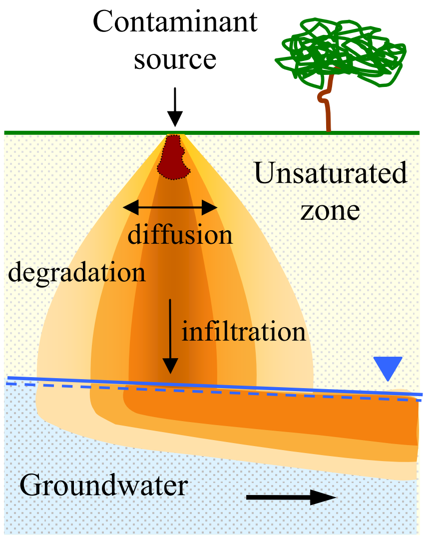


Figure 3.4: Conceptual model for contaminant fate and transport through a homogeneous unsaturated zone.

The solutions in Troldborg et al. (II) were derived based on the following general transport equation:

$$\frac{\partial(R\theta_w + K_H\theta_a)C_w}{\partial t} = \nabla(\theta_w \mathbf{D_w} + K_H\theta_a \mathbf{D_a})\nabla C_w - q_w \frac{\partial C_w}{\partial z} - \theta_w \lambda C_w \qquad (3\text{-}7)$$

where C_w is the solute concentration in the water phase, R is the retardation coefficient, K_H is the dimensionless Henrys constant, θ_w and θ_a are the water and air content, respectively, $\mathbf{D_w}$ and $\mathbf{D_a}$ are the dispersion tensor in water and air, respectively, q_w is the water infiltration rate, and λ is the first-order degradation rate. Eq. (3-7) is the sum of the standard advective-dispersion transport equations for air and water coupled through the phase partitioning expression (Henrys law) $C_a = K_H C_w$.

Eq. (3-7) can be solved analytically for a variety of boundary conditions and can thereby provide simple general solutions applicable for assessing the risk to groundwater from point sources. The transport equation can be modified to specific site conditions (e.g. the infiltration can be neglected for sources under paved areas) and provide solutions for both saturated and unsaturated conditions.

Based on Eq. (3-7), Troldborg et al. (II) provide four analytical solutions for assessing the risk posed by sites contaminated with volatile contaminants: a

3-dimensional solution accounting for infiltration, lateral gas diffusion, sorption and degradation; a simple 1-dimensional screening model, and two one-dimensional radial gas diffusion models for use in simulating volatile organic contaminant diffusion in unsaturated soils with an impermeable cover.

Three of these models were tested on sites contaminated with volatile compounds to evaluate their applicability. It was hereby found that both horizontal diffusive spreading of contaminants in the gas phase and aerobic degradation can substantially decrease the solute concentrations reaching the groundwater table. These results were most sensitive to the water content and especially the degradation rate, while dispersivities only were influential at nearly saturated conditions. Although the 3-dimensional solution provided a more realistic picture of the contaminant spreading in the unsaturated zone, the simple 1-dimensional screening model was found to give a reasonable approximation to the vertical transport for easy degradable compounds and/or at high water contents.

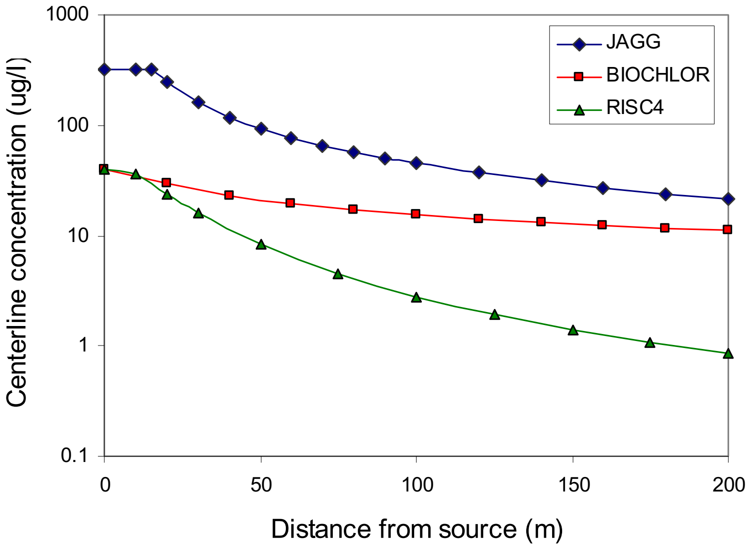
The 3-dimensional model can be attractive for screening purposes as it does not rely on more site-specific input than the traditional 1-dimensional unsaturated zone leaching models. However, an implication of using the 3-dimensional model is that the coupling to a groundwater model becomes more complicated as the concentrations reaching the groundwater impact a larger (radial) area at the groundwater table and thus are not spatially constant (Troldborg et al., II). It should be noted that although the gaseous diffusive transport might lead to a reduced risk from a concentration point of view, the mass discharge reaching the groundwater table is unchanged.

The solutions of Eq. (3-7) are based on several simplifying assumptions that neglect potentially important aspects such as gaseous advection, heterogeneities and the capillary fringe. However, they are still considered very suitable for an initial risk assessment, where the available data often are sparse. The vertical downward transport to groundwater can in some cases be dominated by presence of fractures, especially for clay media. Of the presented tools in Table 3.3, only ConSim can allow for fracture transport by use of a double-porosity module (Davison and Hall, 2003). Other analytical models for fracture transport are available (e.g. Sudicky and Frind, 1984; Sudicky and Frind, 1982) and can be used in risk assessment contexts given that the necessary fracture data are available. A lot of efforts are currently targeted at including fracture transport into the Danish risk assessment tool, JAGG (Chambon et al., 2010; Christensen et al., 2010; Jørgensen et al., 2008)

3.3.3 Saturated zone

The tools presented in Table 3.3 are very similar in the way they model transport in the saturated zone. All of them simplify the groundwater flow as one-dimensional and steady, account for dispersion, can describe biodegradation through first-order kinetics and allow for linear sorption.

Although all the tools account for hydrodynamic dispersion in the aquifer, there is a difference in how the dispersion is modelled and in the default dispersivity expressions. The same is the case for the estimation of the source zone mixing depth in the aquifer. Figure 3.5 shows the steady centreline concentration distribution downstream of a source as calculated by applying a selection of the tools on a case study using the same input. The difference between results is due to the difference in default expressions for calculating dispersion and mixing depth.



Input	Value
Solute source concentration [mg/l]	40
Source width [m]	10
Source length [m]	10
Source depth (or screen length) [m]	2
Hydraulic conductivity [m/s]	5e-5
Hydraulic gradient [-]	8e-3
Effective porosity [-]	0.2

Figure 3.5: Steady-state centerline concentration distribution in groundwater downstream of the source zone calculated with three different risk assessment tools. The calculated concentrations are based on the same input values (shown next to the graph). Note that JAGG assumes that the source concentration is measured in a well-screen of length 0.25 m. If not (as is the case in figure 3.5), the source concentration is corrected to account for dilution in the well-screen.

Degradation is also an important natural attenuation process. Some of the tools in Table 3.3 have an extended description of biological decay. BIOCHLOR can for example simulate sequential degradation of chlorinated solvents and can thus account for the formation of by-products, while BioBalance account for competition effects when evaluation the degradation potential.

3.4 Findings for local scale risk assessment

- Methodologies for risk assessment of groundwater contamination often follow a tiered approach and are thus tailored to the available knowledge level.

- Local scale risk assessments of point sources are usually based on generic standards that directly can be compared to measured or predicted contaminant concentrations throughout the site. Mass discharge-based risk assessments are becoming increasingly popular, but are data demanding and thus considered useful at later stages in a risk assessment.

- Many models for local scale risk assessment are available. Most of the models are conceptually simple and designed for estimating the concentration levels in groundwater using only few inputs and they can thus be applied to many different types of sites.

- A literature review has revealed that the existing tools for local scale risk assessment ignore gas phase transport in the unsaturated zone, although this is known to be a dominant transport mechanism for many compounds. Other limitations of the existing models are that fracture transport is often neglected, that similar local scale models produce different results even with the same input due to in-built features “hidden” from the users and that the models rely on effective parameter values that can be difficult to obtain in practice.

- It is shown how both gas phase transport and degradation in the unsaturated zone can be incorporated into analytical models that can be useful for initial risk assessment purposes.

4 Risk assessment at the catchment scale

Groundwater is an important source of drinking water in many countries. In Denmark, the drinking water supply is almost exclusively based on groundwater extraction. Groundwater is also a vital part of the natural water cycle and provides the base flow of various surface water ecosystems. Protecting groundwater resources and keeping them free from contamination is thus essential. The EU Water Framework Directive (WFD) seeks among other things to ensure good chemical and ecological status of both groundwater and surface waters (European Commission, 2000). The practical implementation of the WFD necessitates the evaluation of all types of contaminant sources within a specific catchment in order to assess their direct impact on water quality and ecosystem health (McKnight et al., 2010). This speaks in favour of carrying out risk assessments of contaminated sites at a catchment scale. The catchment considered can for example be the capture zone for a drinking water supply or the catchment area for a stream. The motivation for carrying out risk assessment at a catchment scale is two-fold: i) initiating action at a site (e.g. remediation) is usually driven by its impact or its possible future impact on a receptor, and ii) the multiple sites located within the catchment can be handled collectively and the risk from each of these sites can be assessed at the same endpoint (i.e. the receptor). The risks from different sites can therefore be compared, which allows prioritising and ranking the many sites within the catchment area. The traditional risk assessment tools are less suitable for prioritisation purposes, because they consider the contaminated sites separately, and focus only on predicting plume concentrations at the local scale (Troldborg et al., I).

Catchment scale risk assessment approaches can in principle be used to evaluate the contaminant impact on any kind of downstream receptors and has for example been used for assessing the impact from a point source on rivers and streams (e.g. Conant et al., 2004; Kalbus et al., 2007; McKnight et al., 2010). Here, the receptor in focus is drinking water supply wells. In order to assure a supply of acceptable drinking water from abstraction wells and to develop Water Safety Plans, the World Health Organisation (WHO) stresses the importance of applying preventive risk management approaches that cover the whole system from the catchment to the consumer (Davison et al., 2004). Numerous studies have furthermore shown the rationale of assessing the risk of contaminated sites based on the impact on the water supply wells in the catchment (e.g. Einarson and Mackay, 2001; Tait et al., 2004a; Frind et al., 2006; Arey and Gschwend, 2005; Troldborg et al., I; Kennedy and Lennox, 1999).

Figure 4.1 shows a conceptual model for the risk assessment of groundwater contamination from a point source within the catchment of a water supply. The pathway considered is the release of contaminants from the point source at local scale, contaminant transport in groundwater from the point source to the water supply well(s) and dilution at the well due to mixing of contaminated water with abstracted clean water. Table 4.1 summarises the source-pathway-receptor concept for catchment scale risk assessment considered here.

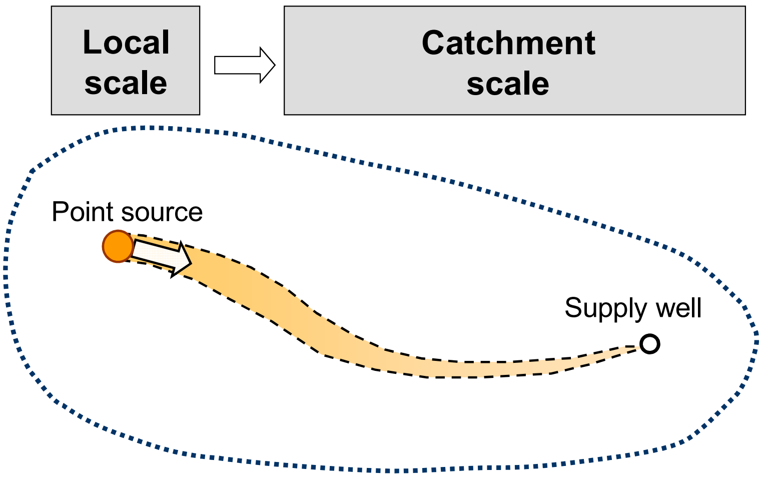


Figure 4.1: Conceptual model for risk assessment of a point source within the catchment of a water supply well (modified from Troldborg et al., I)

Table 4.1: Summary of source-pathway-receptor concept at catchment scale

Source	**Pathway**	**Receptor/output**
Point source	Fate and transport in groundwater	Drinking water supply well
• Documented contamination	• Water	• Concentration
• Data exist	• Soil	• Mass discharge
• Located within catchment		

4.1. Catchment-scale risk assessment approaches

A commonly applied approach for assessing the potential risk for abstracted groundwater at a supply well to become contaminated is the delineation of well-field protection zones. Often different time-of-travel zones are determined displaying the time a contaminant will take to reach the well. These protection zones depend on the contaminant of concern and are usually delineated based on backward particle tracking from the well (i.e. advection-based). The delineation of the catchment and/or other protection zones is a key element in any catchment-scale risk assessment approach, because it decides which contaminated sites pose a potential threat to the well.

The existing catchment-scale risk assessment models can roughly be divided into i) vulnerability based methods that aim at providing maps of the most susceptible areas within the catchment to the well and usually rely scoring-systems, and ii) mass discharge based approaches that aim at calculating the actual (future) contaminant impact on the water supply well from the sources identified in the catchment.

4.1.1. Vulnerability-based methods

Several studies combine well-field protection zones with scoring-based vulnerability mapping methods like those described in section 3.1 (e.g. Nobre et al., 2007; Secunda et al., 1998; Tait et al., 2004b; Somaratne and Ashman, 2007). This is for example done in the Danish system GISP (Danish Regions, 2007), where the catchment areas for supply wells are incorporated in an administrative vulnerability map. In order to prioritise boreholes potentially at risk from chlorinated solvent contamination, Tait et al. (2004b) present a score-based risk assessment methodology that combines groundwater protection zones (50 day zone, 400 day zone and the entire catchment) with chlorinated solvent user industry data and an aquifer vulnerability index.

Frind et al. (2006) developed a well vulnerability concept for investigating the impact of contaminant spills of limited duration within the capture zone of a well field. They use forward and backward transport modelling to generate intrinsic well vulnerability maps displaying different information such as expected contaminant arrival times, dispersion-related reduction in concentration and exposure duration. Frind et al. (2006) focus only on the protective characteristics of the pathway medium. For describing the ability of the pathway medium to dilute a potential contamination and reduce the impact on a supply well, a unit pulse is released at the pumping well within an inverted flow field. A backward-in-time advective-dispersive transport simulation then provides the impact on the well of a unit pulse released anywhere within the capture zone. Enzenhoefer et al. (2010) extended this well vulnerability concept to also account for uncertainties by setting the concept into a probabilistic framework.

Vulnerability approaches are valuable for an initial screening of contaminated sites and can support the identification of critical areas and determine where new investigations should be targeted at. However, most of these methods have a number of limitations (Worrall and Besien, 2005). The scores and weights are typically assigned subjectively and many studies have shown that different scoring-systems can provide substantially different results. Furthermore, the methods do usually not account for actual concentration measurements and often poor correlation between vulnerable areas and actual concentration measurements has been observed. Thus, these methods cannot demonstrate the actual threat to the groundwater resource at either the local scale or at the receptor (Tait et al., 2004b). In order to prioritise the remediation efforts between point sources more site-specific information must therefore be allowed for.

4.1.2. Mass discharge based approaches

Numerous studies have used mass discharge estimates from point sources in order to evaluate how the water quality in the abstraction wells is impacted, as it is the mass discharge that defines the severity of the problem posed by a plume (Feenstra et al., 1996). Einarson and MacKay (2001) present a conceptual framework for risk assessment and prioritisation of contaminated sites in a groundwater catchment. They proposed using mass discharge estimates from the point sources within the catchment to estimate worst-case concentration in the abstracted water at a supply well. Bauer et al. (2004) use a mass discharge approach to identify active contaminant sources and their individual source strength within the catchment for a protection well. They find that the mass discharge abstracted by the protection well could not be attributed to the mass discharge estimated from the identified potential sources and thus conclude that additional point sources might exist within the catchment area.

Table 4.2 presents an overview of existing catchment scale models that all can be used for estimating the contaminant impact on the water supply well. Tait et al. (2004a) presents the Borehole Optimisation System (BOS) for identifying the optimum locations for new supply wells in urban areas. BOS consists of three modules: a catchment zone probability model that uses a 3D groundwater model for a probabilistic delineation of the borehole catchment; a GIS based land use model that utilises historical maps and a land use database to identify past and present surface activities located within the catchment; and a stochastic pollution risk model to estimate the cumulative impact of a chosen contaminant from all identified sources relevant to a water supply well in a given year (Tait et al., 2004a). The applicability of BOS has been demonstrated in two case studies in the UK (Chisala et al., 2007; Tait et al., 2008; Davison et al., 2002).

Table 4.2: Models for catchment scale risk assessment of groundwater contamination.

Models for assessing the contaminant impact on groundwater at catchment scale	Tait et al. (2004)	Arey & Gschwend (2005)	Frind et al. (2006)	Troldborg et al. (I)	Overheu et al. (IV)
General					
Aim/output: Impact on water supply (I) Optimal borehole location (O) Prioritisation of point sources (P)	I O	I	I	I P	I P
Type of point sources considered: Documented contamination (D) Potential contamination (P)	D P	D		D	D P
Multiple point sources	X			X	X
Local scale (source model)					
Mass discharge function: Continuous (C) Decaying (D) Pulse (P)	Continuous	Decaying	Pulse	Continuous; Decaying	Continuous; Decaying
Mass discharge uncertainty	Monte Carlo	Monte Carlo		(Qualitative)	Qualitative
Other features: Sorption (S) Degradation (D)				S D	S D
Source history	X			X	X
Catchment scale					
Hydrogeology	3D groundwater model	Uniform flow field	3D groundwater model	3D groundwater model	3D groundwater model
Catchment delineation	Particle tracking		Backward transport	Particle tracking	Particle tracking
Catchment uncertainty analysis	Stochastic; GLUE				Multiple model simulation
Advection	X	X	X	X	X
Dispersion		X	X		
Degradation:	First-order			First-order; Sequential; 2 zones	First-order; Sequential
Sorption	X	X		X	X
Dilution in supply well	X	X	X	X	X
Impact on supply well: Static (S) Time-dependent (T) Cumulative (C) From individual point sources (I)	T C	S	T	T C I	T C I

Arey and Gschwend (2005) present a screening model to anticipate well water concentrations and transport times for gasoline constituents (LNAPL) migrating from underground fuel tank releases to typical at-risk community water supply wells. Their approach uses mass discharge calculations based on average contaminated site conditions in the United States, and the uncertainty of the predicted contaminant levels in the supply well is evaluated stochastically.

Troldborg et al. (I) present the CatchRisk model for assessing the risk and prioritising contaminated sites within the catchment for a water supply. CatchRisk combines site specific transient mass flux estimates from all known point sources at the local scale with simple catchment scale transport and fate simulations in a complex 3D groundwater system. The source model at local scale is designed to be flexible so that it can be tailored to the different types of point sources within the catchment as well as possible, because these sources may vary considerably in complexity and in data availability. CatchRisk was tested on a catchment area near Copenhagen, Denmark. Hereby, an integrated overview of the identified point sources in the area was provided and the sources most likely causing the observed contamination at the waterworks were identified. The method was found to be valuable as a basis for prioritising point sources according to their impact on groundwater quality.

The concept from Troldborg et al. (I) was extended by Overheu et al. (IV) to incorporate an initial screening step based on a modified version of the Danish aquifer vulnerability method GISP, an uncertainty estimation step as well as a score-based prioritisation system (see Figure 4.2). The uncertainty analysis considers i) the uncertainty in the catchment delineation by implementing different conceptual interpretations of the geological stratification as well as investigating the influence of historically varying abstraction rates, and ii) the uncertainty in the mass discharge estimates through a score-based system. The prioritisation system is flexible and assigns scores based on factors such as magnitude and duration of contaminant impact on the supply well, and the uncertainty related to both the mass discharge estimate as well as to whether the site is located within the catchment. The applicability of the method by Overheu et al. (IV) has been evaluated on two catchment areas in Denmark (Capital Region of Denmark, 2009; Region Zealand, 2010).

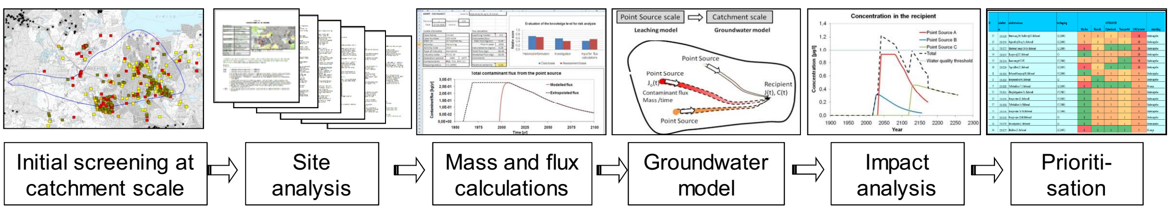


Figure 4.2: General elements of the concept used in Overheu et al. (IV).

Figure 4.3 illustrates the general concept behind the risk-based prioritisation approaches presented in Troldborg et al (I) and Overheu et al. (IV). In the area near a water supply well several point sources might have been identified as potentially or definitely contaminated. By use of conventional risk assessment tools it might be found that some of these sites constitute a risk to groundwater at local scale (black dots), while others do not (white dots). Ideally, all the black dots should be removed, but due to the limited resources we can only afford to remediate a few of these sites within the nearest future. Following the traditional risk assessment one might choose to remove the sites, where the highest concentrations have been measured or predicted at local scale. However, other aspects might be just as decisive, e.g. the amount of contaminant mass released from the point source to groundwater over time and whether and to what extent the water supply is affected. By applying a catchment-scale approach the point sources located within the capture zone (and thus pose a potential threat to the water supply) are identified and their impact on the abstracted water at the supply well can be estimated. Hereby, the impact from the different sites within the capture zone can be compared allowing for a better prioritisation of the point sources in order to assure the abstracted groundwater at the supply well.

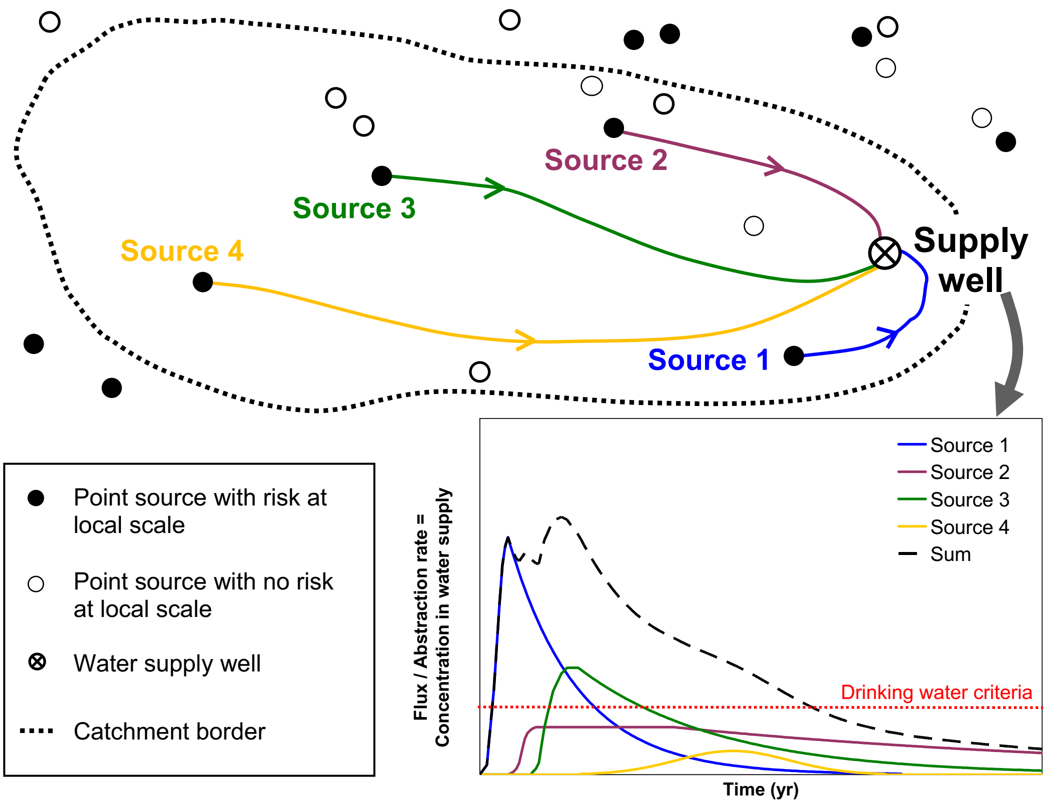


Figure 4.3: Concept of risk-based prioritisation of point sources at catchment scale.

Although catchment scale risk assessments based on mass discharge estimates have demonstrated to be very useful for various applications, there are still limitations to these types of approaches. The calculation of transient mass discharge estimates from the possibly numerous point sources in the catchment is in most practical cases very difficult and prone to large uncertainties due to the often limited available data. The release of contaminants from the source over time is an unknown function and the available field data typically only allow for representing a snapshot of this possibly complex source depletion function. In catchment scale risk assessments, the mass discharge estimation relies on simple source depletion models like the ones presented in section 3.3. The appropriateness of the simple leaching models has been evaluated by comparing them to more advanced numerical simulators and is the focus of substantial research (see section 3.3).

The catchment scale considerations typically require a groundwater model that can simulate the flow patterns satisfactorily in the catchment area. This groundwater model also relies on many simplifying assumptions and is thus prone to inherent uncertainties (more on this in chapter 5). In all the presented catchment scale risk assessment approaches, steady-state conditions are assumed meaning that for example infiltration and abstraction rates are fixed throughout the modelling period. Although Reilly and Pollock (1996) show that temporal variations in recharge in many cases is insignificant for the capture zone delineation, the temporal varying pumping rate, position, and/or number of active abstraction wells in the catchment can be critical.

Another limitation of the catchment scale approach is that the results can be very difficult to validate in practice. The catchment scale risk assessment model attempts to relate the mass discharge from identified contaminated sites directly to the observations at the water supply. However, though records of concentration over longer time periods might exist for the supply wells, the transient mass discharge estimates from the point sources are usually calculated based on relatively recent site investigation data. These estimates only represent the contaminant situation from the time of the investigations and onwards. In many cases it is therefore not possible to compare the calculated mass discharge from a point source directly to the measured concentrations at the water supply due to the transport time through the catchment. This time delay induce a knowledge gap that can be resolved only by having either past site data or future measurements at the waterworks, or by making some very strong assumptions about the source and its temporal behaviour (release function, time of spill and location).

In order to compare the mass discharges from the point sources with the abstracted mass discharge at the supply well, the mass discharge from the point source needs to be extrapolated back in time (e.g. as in Fig. 4.4). This was for example done when applying the model from Overheu et al. (IV) to a catchment north of Copenhagen, Denmark (Capital Region of Denmark, 2009). To carry out the extrapolation it is assumed that only the mass in the source changes and all other conditions at the site are similar to the investigation time. Although this back-extrapolation in time is questionable and highly uncertain, a fairly good agreement was found between the simulated and observed mass discharges at the waterworks.

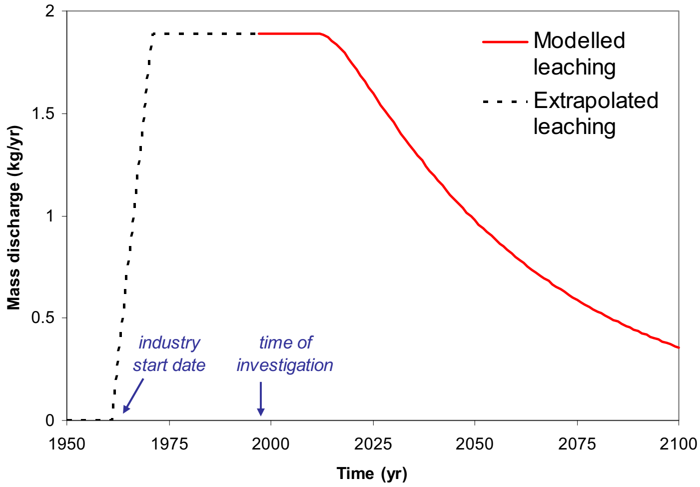


Figure 4.4: Extrapolation of mass discharge from a point source back in time (from the time of investigation to the time at which activities were initiated at the site).

BOS assumes that the mass discharges from the different sites are continuous during the time the industry has been active at the given site. A site will therefore only affect the borehole in a given target year, if this year falls between the industry start date plus the travel time to the borehole and the industry stop date plus the travel time to the borehole (Chisala et al., 2007; Tait et al., 2004a). Different studies have attempted to validate the results from the BOS approach and these studies generally find satisfactory agreement between observed and modelled concentration values in various boreholes (Chisala et al., 2007; Davison et al., 2002; Tait et al., 2004a; 2008).

A major constraint in applying catchment scale risk assessment approaches is the considerable workload related to the collection and interpretation of huge volumes of data from the many individual sites as well as from the catchment. These data are often spread among several parties and stakeholders making the data collection both difficult and time-consuming. The catchment scale simulations require the use of a groundwater model. If such model is not available it needs to be constructed and calibrated, which further adds to the burden of labour.

4.2 Findings for catchment scale risk assessment

- Catchment scale risk assessments can be applied at different knowledge levels ranging from index-based vulnerability mapping to mass discharge based approaches.

- Vulnerability-based assessment is useful for an initial screening of the catchment and the contaminated sites within it, while the mass discharge based approaches are mainly considered applicable at later stages in a catchment scale risk assessment.

- Capture zone delineation plays an important role in any catchment scale risk assessment and a proper groundwater model is therefore essential.

- Catchment scale risk assessments have several advantageous features that may be valuable for decision support within a catchment. Possible outputs are: prioritisation of identified point sources within a catchment; identification of point sources that are most likely to cause contamination at the water supply or that might be problematic in the future; identification of unknown contaminated sites in the catchment; and elucidation of where more information is needed to improve the analysis.

- Catchment scale risk assessments are potentially very time-consuming due to the large efforts required for reviewing many different sites at very different knowledge levels and setting up a groundwater model.

- Although studies have shown a satisfactory agreement between observations and the results from catchment scale risk assessment models, these results are generally very difficult to validate and subject to large uncertainties due to the incorporation of several assumptions and the often limited data available.

5 Uncertainties in risk assessments

Any model is only an approximation of the complex real-world system and so model-based risk assessments are inherently uncertain (Walker et al., 2003). All models are essentially wrong and will be rejected if investigated in sufficient detail and/or if assessed against strict enough performance criteria (Beven, 2002). This is particularly true when the aim is to predict beyond the range of available data, e.g. possible future impacts (Ferguson et al., 1998; von Krauss et al., 2005; Refsgaard et al., 2006). But models are often useful, because they provide reasonable approximations of reality. It is therefore important to assess uncertainty when applying risk assessment models.

Despite its importance, uncertainty is seldom considered in risk assessments of groundwater contamination from point sources (Ferguson et al., 1998). Indeed, most of the current risk assessment tools do not include uncertainty considerations at all (c.f. Table 3.3). Typically uncertainties are accounted for by incorporating conservative assumptions throughout the risk assessment process. The risk assessment is thus based on a precautionary principle to account for the often inadequate available data, the poor conceptual understanding of the system and model ignorance. However, by assigning conservative values to all inputs in a risk assessment model, the outcome is often highly improbable. It is important that risk assessments are not overly conservative since this may result in the needless use of funds to clean-up contamination posing a minimal environmental threat. A proper characterisation of uncertainty is essential in order to produce a reliable and transparent risk assessment and can lead to better decision making (Cushman et al., 2001).

The following sections describe how uncertainty manifests itself in models generally, then how uncertainty can be characterised for local scale mass discharge estimation for individual contaminated sites, and concludes by examining uncertainty in catchment scale risk assessment.

5.1 Uncertainty terminology and definitions

Uncertainty means different things to different people and is often confused with related terms such as error, risk and ignorance (Beven, 2009b; Ferguson et al., 1998). While error can be seen as the deviation from reality (the true state), uncertainty usually arises because we do not know what the true state is. This implies that uncertainty is a statement of confidence and thus is subjective.

Different people will reach different conclusions about how uncertain something is, depending on their own experience, worldview, and the quantity and quality of information available to them (Brown, 2004; Heuvelink et al., 2007; Refsgaard et al., 2006). From the above it follows that the true state must be known if we wish to estimate errors. As the true state is never known for real field applications, error estimation is limited to hypothetical studies, where a modelled simulation is used as the true state of the system. It also follows that expressing and reporting risk assessment results with uncertainty bounds does not necessarily guarantee that the truth is encompassed, because the uncertainty could be based on wrong judgement as a result of ignorance (Refsgaard et al., 2007). Thus, there is no unique solution to representing and estimating uncertainties. In some sense it does not matter how the uncertainties are estimated as long as the assumptions behind the uncertainty analysis are clearly stated (Beven, 2009b).

Walker et al. (2003) present a framework providing a general holistic view of uncertainty in model-based decision support. They characterise uncertainty as being three-dimensional and discriminate between:

- **The location of uncertainty** which refers to the sources of uncertainty i.e. where the uncertainty manifests itself within the model complex. Walker et al. (2003) identifies five locations that apply to most models: context, model structure, parameters, inputs and model outcome. The different sources of uncertainties in risk assessment of groundwater contamination and methods for addressing them will be briefly described in later sections (5.1.1-5.1.3).

- **The level of uncertainty** which describes where the uncertainty manifests itself on the spectrum between the unachievable situation of full determinism and total ignorance, where nothing is known. The different levels of uncertainty are illustrated in Figure 5.1 and consider:

    - *Statistical uncertainty* where all possible outcomes and their individual probabilities are (assumed) known. This is also termed bounded uncertainty (Brown, 2004; Refsgaard et al., 2007). Uncertainties are most often addressed using statistical analyses in natural sciences even though such an approach often cannot be justified (Walker et al., 2003).

o *Scenario uncertainty* where the possible outcomes are known, but their associated probabilities are not. In this situation we often have to rely on scenario analyses, a commonly applied approach to the prediction of future impacts and events.

o *Ignorance* where neither probabilities nor the range of possible outcomes can be defined. This situation occurs when there is a lack of awareness that knowledge might be wrong or imperfect and/or because there are fundamental errors in the description of system mechanisms and functional relationships being studied, e.g. chaotic system properties. In this situation the scientific basis for the development of scenarios is therefore weak (von Krauss, 2005). Total ignorance is at the extreme end of the scale of uncertainty, where we do not even know what is unknown (Walker et al., 2003).

- **The nature of uncertainty** which includes i) epistemic uncertainty where the uncertainty is due to lack of knowledge and thus can be reduced, and ii) aleatory uncertainty caused by inherent variability and randomness in the behaviour of the natural system being studied. Such uncertainty cannot be reduced or eliminated (Beven, 2009b; von Krauss and Janssen, 2005; Walker et al., 2003).

Figure 5.1: Level of uncertainty (from Krayer von Krauss & Janssen, 2005)

In the following sections, the types of uncertainties in risk assessment of groundwater contamination from point sources will briefly be explained and characterised using the framework of Walker et al. (2003). Focus will be placed on the location/sources of uncertainty.

Since risk assessments of groundwater contamination often attempt to predict impact based on an extrapolation of available data in time or space, the related uncertainty will usually be at the level of scenario uncertainty and/or ignorance. Ignorance could be due to the adverse effects of a (new/unknown) compound or to undiscovered contaminated sites. For identified point sources it is often possible to describe the level of uncertainty using scenario analyses, because it is possible to characterise the range of possible outcomes (from no exposure to an extreme maximum).

5.1.1. Model context

The model context refers to the conditions and circumstances that underlie the choice of the system delimitation, and the framing of the problems to be addressed within the confines of this system. The context is important to decision support as it clarifies the issues to be addressed, the outcomes of interest as well as the acceptable degree of accuracy of the outcomes (Refsgaard et al., 2007; Walker et al., 2003). The uncertainty in model context, though important, is beyond the scope of this thesis. However, the development of the catchment-scale risk assessment model presented in Troldborg et al. (I) was based on a close dialogue with different stakeholders and regulators and their views have been accounted for during the entire process. The involvement of stakeholders is a way of avoiding controversy when defining model context (Walker et al. (2003)). To this authors knowledge there are no examples in the literature where context uncertainties have been evaluated for risk assessments.

5.1.2. Model structure

Model structure uncertainty is the uncertainty related to the conceptual model. Every model has its foundation in a conceptual model, which is based on how we decide to represent and simplify the system under study. The conceptual uncertainties in risk assessments are due to incomplete understanding as well as the simplifications required to describe complex phenomena such as heterogeneous geology, hydrogeology and contaminant source distribution, transformation processes etc.

Conceptual uncertainties are difficult to quantify, because they often cannot be described statistically or be separated from other sources of uncertainty. Despite many studies showing that the uncertainty in conceptual models is far more dominant than model parameter uncertainty, it is often neglected (Konikow and Bredehoeft, 1992; Neuman and Wierenga, 2003; Højberg and Refsgaard, 2005). In models for risk assessment conceptual uncertainty greatly affects predictions, because the models often describe the system in a very simplified way and rely on scarce data. Usually risk assessment of groundwater contamination is based on only a single conceptual model.

However, uncertainty and ignorance mean that a variety of conceptual models may describe the system equally well (Beven, 2005). Selecting the appropriate conceptual model(s) is a critical decision and one of the most difficult tasks in the modelling process, especially when only little data is available to support the model choice.

Bredehoeft (2005) describes the role of surprise in conceptualization and gives numerous examples, where surprises have occurred and changed the conceptual model. He defines the element of surprise as the collection of new information that invalidates the original conceptual model and entails a completely new paradigm shift. Surprises occur as a result of ignorance (the things we do not know). The element of surprise will always be present, but the chance of a surprise occurring is higher when there is less data available.

One way of addressing conceptual uncertainty is by using multiple model simulations, where a number of plausible conceptual models are set up (and calibrated if data are available) to represent the system under study. The difference between the results of the accepted conceptual models can then be seen as an expression of the overall conceptual uncertainty (Refsgaard et al., 2006). The output from the different conceptual models can also be combined, through Bayesian model averaging (Hoeting et al., 1999; Neuman, 2002; Rojas et al., 2008; 2009; Troldborg et al., III). For example, multiple model simulation has been used to account for different geological interpretations of the same aquifer system (Højberg and Refsgaard, 2005; Rojas et al., 2008; Overheu et al., IV; Troldborg et al., 2007) and to account for geological interpretations in combination with alternative source zones (Cypher and Lemke, 2009; Sohn et al., 2000; Troldborg et al., III).

The use of multiple conceptual models can be seen as a more robust way of handling surprises related to conceptual model uncertainty. This approach to conceptual uncertainty is described as scenario uncertainty in the framework of Walker et al. (2003). However, the multiple model approach only allows for an incorporation of the conceptual models we can perceive and important plausible models might be overlooked due to ignorance. New data could therefore still result in surprises leading to rejection of some of the conceptual models and/or formulation of new conceptual models.

5.1.3. Input and parameter uncertainty

The number and types of model inputs and parameters depend on how the system is conceptualised and are thus directly related to the model structure. Inputs are system data that drive the model (such as climate data or pumping rates), while parameters are intended to represent intrinsic characteristics of the location (or of a process), where the model is applied (Beven, 2009b; Refsgaard et al., 2007). The distinction between inputs and parameters can be somewhat confusing, because a quantity with the same name might be considered a parameter in one model, but an input in another. For example, the hydraulic conductivity is sometimes considered a parameter that is adjusted in an attempt to match simulations and observations of e.g. water level. However, in many risk assessment models (like the ones presented in Table 3.3), where the output entirely relies on the data fed to them, the hydraulic conductivity is considered an input and is not calibrated.

Both model inputs and parameters have uncertainties that are strongly related to the available measurements. Not only are the data in risk assessments (and in many other model applications) usually very limited, they also contain errors. Furthermore they only represent values at particular locations (points), scales, time spans and periods (snapshots) and so are often not related to the parameter or input values actually needed in the model, even though they may have the same name (Beven, 2009b). For example, hydraulic conductivities are often measured on small soil samples and can vary orders of magnitude over short distances. However, most risk assessment models assume homogeneous aquifer conditions in the entire domain and thus require an effective hydraulic conductivity value that represents a much larger volume. This is referred to as the incommensurability issue (Beven, 2009b). Besides being affected by inadequate data, parameter uncertainty also originates from model structure where the model might be over parameterised and the parameters highly correlated.

Because of the limited data available, it is often necessary to resort to input or parameter values from the literature or data extrapolated from other (similar) sites. When doing this, it is important to be aware of the site conditions from which the values are extrapolated, because these might stem from calibration of a different type of model, represent a different scale etc.

The uncertainty associated with model inputs and parameters are usually treated as statistical uncertainty. The literature includes several examples where the influence of input and parameter uncertainty has been investigated for risk assessment models (see section 5.2).

5.2 Methods for quantifying uncertainty in risk assessments

A large number of methods are available for quantifying uncertainties in model simulations (see reviews in e.g. Beven, 2009a; Blasone, 2007; Matott et al., 2009; Refsgaard et al., 2007; Saltelli et al., 2006; Zadeh, 2005). These methods can be roughly divided into two groups depending on whether data exists for model calibration or not. In the following, different methods for the particular problem of estimating uncertainties in risk assessments are briefly described. Note, however, that it is beyond the scope of this thesis to present a comprehensive overview of all available methodologies for uncertainty assessment and propagation.

5.2.1 Uncertainty in risk assessment modelling without historical data

In risk assessments of groundwater contamination it is often necessary to make predictions without being able to calibrate or condition the model against historical time series of observations. In such cases, the output of the risk assessment depends entirely on the chosen input values and the prior assumptions made by modeller regarding model structure(s), parameter values and boundary conditions (Beven, 2009c).

One way to evaluate how the output of a risk assessment model depends on the variation of input and parameters is by conducting a sensitivity analysis (Saltelli et al., 2000). A sensitivity analysis can identify which inputs and parameters the risk assessment is most sensitive to and can thus reveal where efforts and data collection should be targeted in order to reduce the output uncertainty. Different types of sensitivity analysis can be carried out (Blasone, 2007). A local sensitivity analysis investigates how the model output changes relative to the change in each input parameter while keeping all the other inputs at a fixed level. Global sensitivity analysis attempts to evaluate the output sensitivity due to the uncertainty in the input variables, both singly and in combination with one another. Different approaches for global sensitivity analysis exist such as variance-based sensitivity analysis (e.g. Sobol, 2001), generalised sensitivity analysis (e.g. Spear and Hornberger, 1980) and the method of Morris (Morris, 1991). Sensitivity analyses are widely applied in modelling studies, also in risk assessments (a few examples are given in Table 5.1).

The uncertainty of the model output due to parameter and input uncertainties can be addressed using a forward uncertainty analysis (Beven, 2009c). In this approach the uncertainty of the input parameters is specified as a range of possible values together with a function expressing the probability of the different values within the range. The uncertainties in the input parameters are then propagated through the model to produce an overall (probability) distribution of the model results. The propagation of the uncertainty is typically conducted using either probabilistic methods such as Monte Carlo simulation (e.g. Brown and Heuvelink, 2007), first- and second-order reliability methods (FORM/SORM) (e.g. Ditlevsen and Madsen, 1996) and moment analysis (e.g Andricevic and Cvetkovic, 1996) or possibilistic methods such as fuzzy approaches (e.g. Zadeh, 2005). The literature includes several publications where forward uncertainty analysis has been applied to models for risk assessment of groundwater contamination (see Table 5.1).

Table 5.1: Overview (not exhaustive) of uncertainty methods applied in risk assessment of groundwater contamination from point sources. Note that catchment scale risk assessment refers to studies that have investigated the contaminated site impact on abstraction wells.

Method		**Local scale**	**Catchment scale**
Sensitivity analysis		Avagliano et al. (2005) Thornton et al. (2001) Volkova et al. (2008)	Arey & Gschwend (2005) Chisala et al. (2007) Tait et al. (2008)
Forward uncertainty analysis	FORM/ SORM	Hamed et al. (1995; 1996a; 1996b) Hamed & El-Beshry (2006) Lemming et al. (2010) Unlu et al. (1995)	
	Fuzzy/ possibilistic approaches	Baudrit et al. (2007) Guyonnet et al. (1999) Kumar et al. (2006)	Nobre et al. (2007) Zhang et al. (2009)
	Monte-Carlo	Bobba et al. (1995) Guyonnet et al. (1999) Hamed et al. (1995; 1996a; 1996b) Kuber & Finkel (2006) Unlu et al. (1995)	Arey & Gschwend (2005) Chisala et al. (2007) Lemke & Bahrou (2009) Tait et al. (2004a; 2008)
Scenario analysis	Multiple conceptual models	Bobba et al. (1995) Sohn et al. (2000)* Troldborg et al. (III)*	Overheu et al. (IV)
Inverse modelling	Nonlinear regression	Barlebo et al. (1998)* Batlle-Aguilar et al. (2009)* Sonnenborg et al. (1996)* Tiedeman & Gorelick (1993)*	
	Bayesian/ maximum likelihood approaches	Gaganis & Smith (2008)* Schwede & Cirpka (2010)* Sohn et al. (2000)* Troldborg et al. (III)*	
	GLUE		Tait et al. (2004a)*

* In these studies, data have been used to condition the model output uncertainty.

Critical for all the above methods is the prior assumptions made regarding what elements in the model that are considered uncertain and how the uncertainty is represented. It can often be difficult to specify prior probability density functions (pdf) for the various model input parameters, especially when the parameters are correlated. Furthermore, the choice of a proper sampling strategy will influence model results if the number of uncertain parameters is high (Beven, 2009c).

5.2.2 Uncertainty in risk assessment modelling with historical data

The uncertainty quantification methods described in section 5.2.1 can also be used in situations, where data are available for calibration. However, the addition of data makes it possible to evaluate the performance of the models used, and to calibrate the model outcomes to historical data. Data and available observations can therefore be used to constrain model uncertainty and parameters. Many approaches have been developed for this purpose (see e.g. Beven, 2009a; Blasone, 2007; Yeh, 1986).

A problem often encountered in the calibration of environmental models is that of non-uniqueness, i.e. the fact that several sets of parameter values (as well as model structures) can produce equally good fits to the observations. This is particularly the case with models that are over-parameterised and/or where the model parameters are strongly correlated (Beven, 2009a). Non-uniqueness contributes to uncertainty, because equally good parameter fits to historical data can produce widely different model predictions.

In groundwater modelling, parameter and output uncertainties have often been estimated by use of inverse methods like the nonlinear regression approach (e.g. Doherty, 2005; Hill and Tiedeman, 2007) and Monte Carlo-based techniques such as Bayesian uncertainty estimation and Generalized Likelihood Uncertainty Estimation (GLUE) (Beven and Binley, 1992). Table 5.1 presents an overview of inverse methods applied in risk assessment of contaminated sites. Note that Table 5.1 is not exhaustive and that other inverse methods are also available.

5.2.3 Bayesian approach to model conditioning

In the following, the Bayesian approach to the inverse problem will briefly be described as this is a widely applied approach for uncertainty estimation and also was used in Troldborg et al. (III). The Bayesian approach can be seen as a learning strategy, where the probability of a model output is updated every time new data become available. Given a set of feasible models **M** (hypothesis) and some observations **O** (evidence), the probability of the model output given these observations can be determined using Bayes theorem:

$$\Pr(\mathbf{M}|\mathbf{O}) = \Pr(\mathbf{O}|\mathbf{M})\Pr(\mathbf{M})/C \tag{5-1}$$

$\Pr(\mathbf{M}|\mathbf{O})$ is the posterior probability of the model outputs given the observations, $\Pr(\mathbf{M})$ is the prior probability of the model outputs, $\Pr(\mathbf{O}|\mathbf{M})$ is the so-called likelihood function which quantifies how well the model reproduces the available data, and C is a normalizing constant ensuring that the area under the posterior distribution is unity.

The Bayesian approach requires the specification of model uncertainty a-priori based on best judgment, and then updates this uncertainty once data become available. It has the advantage of providing predictive probability distributions of the variables of interest and enables the comparison and combination of different model structures (Beven, 2009a).

The prior distributions can be subjectively chosen based on for example expert opinion, literature values and experiences from similar studies. If only limited data are available these choices will become critical. However, as stated by Freeze et al.: "*it seems right and proper to allow for the experience gained at other sites, or the implications that can be gleaned from "soft" data at the site, to play a role in reducing uncertainty*" (Freeze et al., 1990).

The selection of a proper likelihood function is vital for the application of the Bayesian approach (as well as in GLUE) and is a somewhat controversial issue (Beven, 2009a; Beven et al., 2008; Mantovan and Todini, 2006; Stedinger et al., 2008). The likelihood function quantifies the mismatch between model predictions and the observed data (the residuals), which usually are assumed to follow a simple Gaussian distribution. However, the residual distribution is often a complex function due to the various sources of uncertainty and defining a likelihood function reflecting all these uncertainties can be very difficult.

5.3 Mass discharge uncertainty

In this section the uncertainty related to mass discharge estimation from contaminated sites at local scale is described. The mass discharge uncertainty also constitutes a vital input for the catchment scale risk assessment. Section 5.4 addresses catchment scale uncertainty.

5.3.1 Uncertainty of mass discharge across multi-level control plane

The uncertainty of estimating the mass discharge passing a multi-level sampling network has been explored in both synthetic and field studies (see Table 5.2). The advantage of the synthetic studies is that the results can be compared to a synthetically generated true mass discharge from which the relative mass discharge *error* can be quantified. Li et al. (2007) and Schwede and Cirpka (2010) use this approach to evaluate the applicability of their proposed methods for quantifying mass discharge uncertainty. The method presented in Troldborg et al. (III) was also tested and validated on a synthetic case in Troldborg et al. (2010).

For field studies, the true mass discharge is unknown, so here the relative mass discharge *uncertainty* (i.e. standard deviation divided by mean) is calculated instead (see Table 5.2). Both the relative mass discharge error and uncertainty was quantified in the study by Schwede and Cirpka (2010).

The main motivation for most of the studies in Table 5.2 is to investigate the number of sample points required to obtain reliable mass discharge estimates. Li et al. (2007) find that in cases with little source mass removal and full breakthrough at the control plane, a sampling density (defined in Table 5.2) of 1% or higher is adequate for an accurate mass discharge estimate (i.e. less than 20% error). Their study considered a relatively homogenous situation. When the aquifer or the concentration distribution becomes more heterogeneous the errors might be significantly higher. Kubert and Finkel (2006) find that the spatial sampling interval at the control plane should be similar to the spatial correlation length scales of the hydraulic conductivity field to reduce the estimation errors. They conclude that the widely used approach of interpolating point measurements of hydraulic conductivity and concentration provides poor mass discharge estimates for heterogeneous aquifer situation.

It is interesting to note that although both Schwede and Cirpka (2010) and Troldborg et al. (III) use low sampling densities, they still provide fairly narrow uncertainty bounds. The reason for this is that in the study by Schwede and Cirpka (2010) the mass discharge is also conditioned on the true boundary conditions (the same as having perfect knowledge of the source zone and hydraulic boundaries), which clearly will constrain the uncertainty/error bounds. In Troldborg et al. (III) the boundaries are not known and are instead represented by multiple conceptual models based on site investigations. This means that although the number of sampling points at the control plane is low, data obtained from site investigations outside the control plane have also been incorporated into the applied model set-up and therefore help constraining the uncertainty. It should also be noted that the distance from the source zone to the control plane in Troldborg et al. (III) is much larger than in the previous studies. The larger distance is likely to give a more smooth spatial concentration distribution at the control plane and could explain why the relative mass discharge uncertainty obtained is comparable to the other studies despite the low number of sampling points.

Table 5.2: Uncertainty of mass discharge estimates based on multilevel sampling at different sampling densities, degree of heterogeneity and control plane locations for a (assumed) steady contaminant plume situation. The uncertainty is given as relative error for the synthetic studies and relative uncertainty (standard deviation/mean) for field studies.

Reference	a) Kubert & Finkel (2006)			Li et al. (2007)		Beland-Pelletier et al., submit.	Troldborg et al. (III)	Fraser et al. (2008)	Schwede & Cirpka (2010)	
No. of sampling points	32	40	40	9	25	80	28 b)	210	9 b)	
Control plane area (m^2)	60	80	80	77		160	2800	30	250	
Sample support (m^2) c)	0.063			0.09			0.5		0.1	
Sampling density (%) d)	3.3	3.1	3.1	1	3		0.5		0.4	
Mass discharge relative uncertainty (%)						40	~50	12	76	80
Mass discharge rel. error (%)	~15	~40	100	20	10				61	2
Variance of lnK	0.25	1	2	0.29		0.29	~2.5	0.29	1	
Distance to control plane	22.5			4		40	160	2.7	16	33
Synthetic study (S) Field study (F)	S			S		F	F	F	S	
Data type: Hydraulic conductivity (K) Head (h) /gradient (i) Concentration (C)	K C i			K C i		K C i	K h C	K C i	h C	
Overall approach used e)	GMC			JGC		EP	IGM	EP	IGM	

a) The mass discharge error is here determined at many different sampling densities.

b) Mass discharge uncertainty is also conditioned on measurements up/downstream of the control plane as well as on the boundary conditions.

c) Sampling support: the area that the measurement is assumed to represent (usually the grid cell size).

d) Sampling density: number of sample points times sampling support divided by the control plane area.

e) GMC: Geostatistical Monte Carlo simulation; IGM: Inverse geostatistical modelling; JGC: joint geostatistical conditional simulation; EP: Error propagation.

5.3.2 Uncertainty of transient mass discharge estimates

The studies in Table 5.2 provide insight into the expected uncertainty in the estimation of mass discharges in the field with respect to number of samples, degree of heterogeneity etc. However, the methods in the table cannot be used to quantify the uncertainty of transient mass discharge estimates determined by local-scale leaching models (c.f. section 3.4.1), because the data to validate and support this kind of calculation are rarely available. In this case, the mass discharge uncertainty can be assessed by use of forward uncertainty analysis or by qualitative approaches.

In the Borehole Optimisation System (BOS) by Tait et al. (2004a), continuous mass discharge estimates through the unsaturated zone to groundwater (using Eq. 3-2) from all potentially contaminated sites in a catchment are determined probabilistically by use of Monte-Carlo simulation. In the application of BOS to two case studies, the mass discharges were estimated assuming the source concentrations to be constant (a fraction of the solubility), while the source area and infiltration rate were treated as random variables (Chisala et al., 2007; Tait et al., 2008).

Troldborg et al. (I) and Overheu et al. (IV) attempt to estimate the transient mass discharges based on measured data at a contaminated site. The related uncertainties are in Overheu et al. (IV) assessed using a scoring system. This qualitative approach is based on a series of questionnaires, where both the historical data and the site investigation data are evaluated. In order to estimate the mass discharge from point sources where no data (i.e. potential sources) or only few data are available a set of default values are used and the estimated mass discharge is assigned the maximum uncertainty score (Capital Region of Denmark and Region Zealand, 2010).

5.4 Uncertainties at the catchment scale

At the catchment-scale, the uncertainties are highly dependent on the groundwater model. This issue will be examined in the next sections. However, the uncertainty at catchment scale is also related to the contaminant degradation rate during the transport from the point sources to the water supply well. For example, Chisala et al. (2007) and Tait et al. (2008) employed a sensitivity analysis to show that contaminant degradation rate during the transport through a catchment was a critical parameter for the predicted concentration at a borehole.

5.4.1 Uncertainty in catchment delineation

The uncertainties related to the groundwater model influence the delineation of the catchment area and the travel times from the contaminated sites to the water supply. The catchment determines which sites are potential threats to the water supply, and a reliable delineation of the catchment boundary is therefore crucial for the final risk assessment and prioritisation. The exact location of the catchment boundary can be particularly important for point sources located close to the simulated catchment boundary.

Although the groundwater model usually can be conditioned to several observations such as hydraulic head, stream discharge and drawdown data from pumping tests, it is likely that many different parameter sets will fulfil a given calibration criteria equally well. Furthermore, model structure is uncertain, especially the interpretation and conceptualisation of hydrogeology in the model and the chosen boundary conditions.

Catchment delineation is often carried out using backward particle tracking methods in hydrological models. To account for the uncertainties in the catchment delineation the macro-dispersion approach presented by Frind et al. (2002) could be applied, where backward advective-dispersive modelling is used to determine probability-of-capture plumes. A probabilistic approach similar to the one employed in BOS (Tait et al., 2004a), which is based on the use of Monte Carlo and/or GLUE, could also be used to account for uncertain model parameters. Monte Carlo based methods have been widely used to obtain probability maps of the spatial distribution of the catchment (e.g. Vassolo et al., 1998; Feyen et al., 2001; 2003; Stauffer et al., 2005; Riva et al., 2006)

The above approaches typically only account for the uncertainties in hydrogeological parameters. However, aquifer systems can be very complex, where multiple and discontinuous geological layers can create complex flow patterns. In practice, such systems are difficult to characterise and conceptualise for groundwater modelling purposes. The uncertainty related to the aquifer conceptualisation has shown to significantly influence groundwater modelling predictions in a way that can not be captured by parameter uncertainty (Højberg and Refsgaard, 2005; Rojas et al., 2008; Troldborg et al., 2007).

The importance of the hydrogeological conceptual model on capture zone delineation and on the catchment-scale risk assessment of a contaminated site was demonstrated in Tuxen et al. (2008). Two conceptual hydrogeological models (A and B) were here formulated for an area around a water supply located north of Copenhagen, Denmark. The conceptual models were based on different interpretations of the stratification of the quaternary deposits and implemented in two different groundwater models as illustrated in Figure 5.2. Geology A is based on a planar structured geology, where an upper and a lower aquifer are separated by a clay layer, while Geology B is represented by inclined and more discontinuous layers.

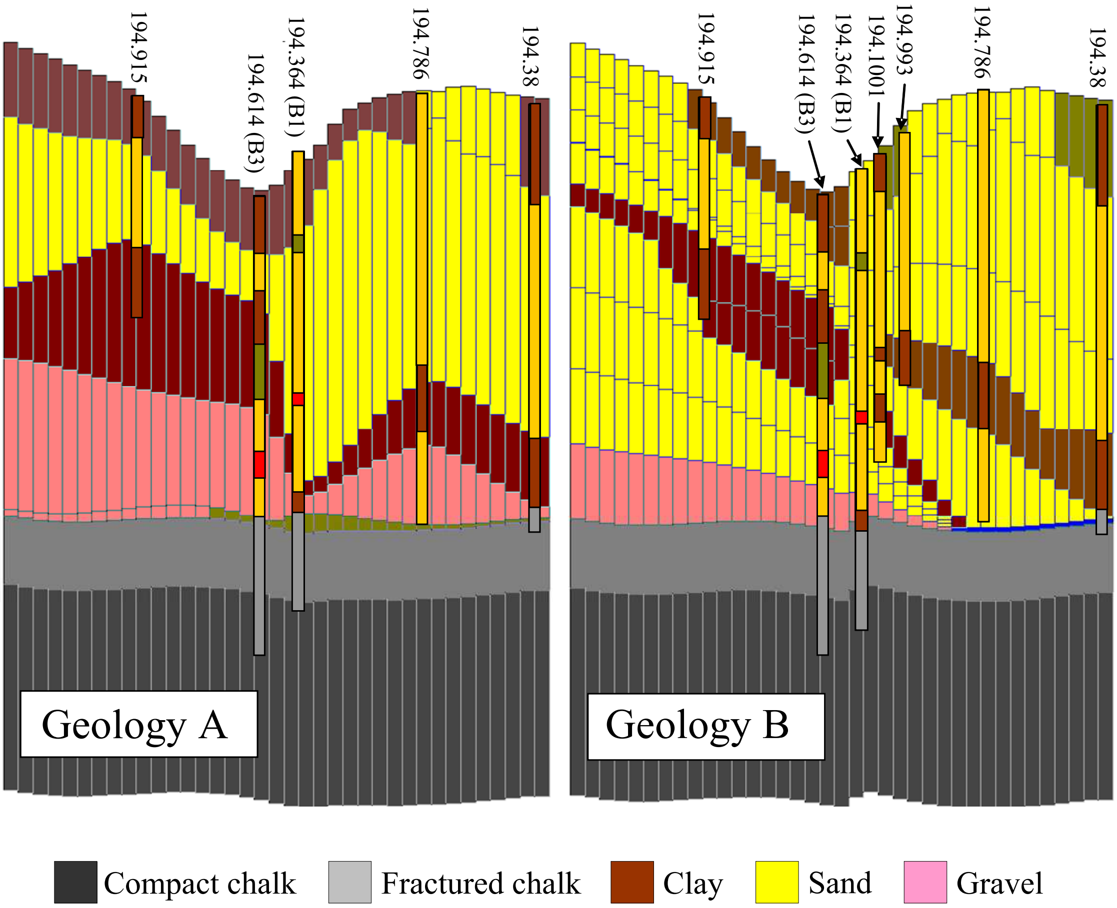


Figure 5.2: The two hydrogeological models (A and B) employed by Tuxen et al. (2008) to show the importance of geology on catchment scale risk assessment. Note that some of the indicated boreholes have been projected onto the cross section and that more boreholes have been used in the interpretation of geology B.

The two groundwater models were calibrated against the same head and drawdown data set and were found to describe the prevailing flow in the area equally well. Particle tracking scenarios were carried out with both groundwater models to investigate the potential transport pathways from a contaminated site located near the water supply. Given the current operation of the water supply wells, both models revealed that a contamination at this site was unlikely to reach the water supply, but instead would discharge into a nearby stream. However, as the water supply had been operated with larger abstraction rates in the past, particle tracking was also carried out using the historical abstraction rate. Hydraulic head data were not available for this past period and it was therefore not possible to validate the obtained flow pattern under historical pumping conditions. The results of the particle tracking were substantially different for the two groundwater models (Fig. 5.3). For model A the particles released at the site were more or less unaffected by the increased pumping rate and ended up in the nearby stream, while Model B predicts that the released particles would enter the water supply through a geological window.

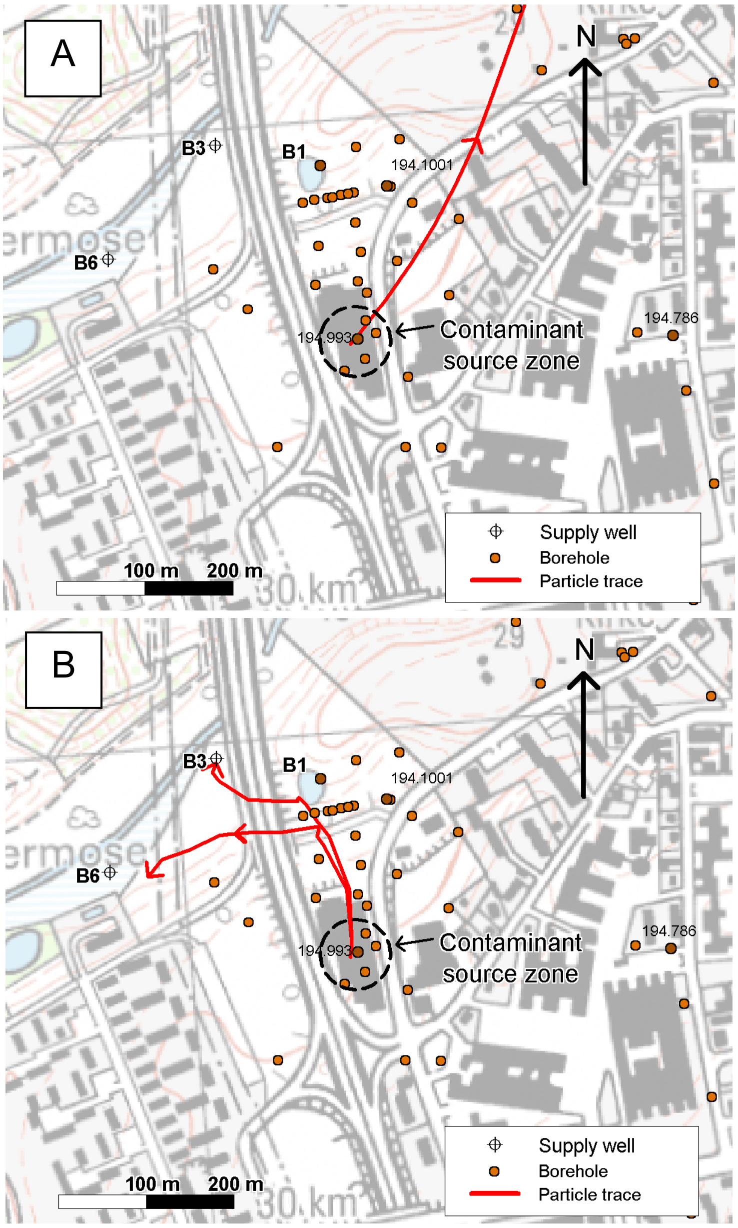


Figure 5.3: Particle traces from a contaminated site during the historical pumping scenario as simulated with model A and B (modified from Tuxen et al., 2008).

The above results show how the uncertainty of the conceptual hydrogeological model can influence the location and extent of a capture zone and therefore also affect the catchment scale risk assessment of contaminated sites. Overheu et al. (IV) propose the use of different hydrogeological interpretations in a set of groundwater models in order to account for the conceptual uncertainties in catchment scale risk assessments. Multiple model simulation is seen as a more robust way to handle the conceptual uncertainty and the use of statistical approaches such as multiple point statistics (Strebelle, 2002) and transition probability geostatistics (e.g. Carle and Fogg, 1997; Weissmann et al., 1999) are increasingly being used to generate multiple conceptual geological models.

5.4.2 Uncertainty in prioritisation of point sources at catchment scale

It is clear that the uncertainties in both the mass discharge estimation at the local scale and in capture zone delineation can greatly affect the prioritisation of contaminated sites at the catchment scale. These uncertainties need to be accounted for in order to carry out a more robust prioritisation. Overheu et al. (IV) attempt to do so by using a systematic scoring system that is tailored to the concerns of the specific catchment area. The system classifies and ranks the identified sites by assigning weights to different factors such as the magnitude and duration of the calculated mass discharge, the travel time from the site to the water supply, and the uncertainty in both the estimated mass discharge and the capture zone delineation. Although this scoring system is simple, it does provide good indications of the sites where the uncertainties are expected to be the largest and where more investigations are thus needed. However, it should be noted that the resulting prioritisation is highly dependent on the subjectively assigned scores and it is recommended that these scores are determined in consultation with the authority responsible for the catchment of concern.

5.5 Findings for uncertainties in risk assessment

- Risk assessments are subject to data limitations that hamper the specification of model input and the selection of appropriate model structure.

- Risk assessments are subject to many sources of uncertainty. Conceptual model uncertainty and lack of system understanding is demonstrated to have a large impact on risk assessments at both the local scale and catchment scale.

- The predictions made in risk assessments can often not be validated against data and the results therefore depend entirely on the input entered. Forward uncertainty approaches, sensitivity analyses and qualitative approaches are possible options for evaluating the uncertainty in these situations.

- Methodologies have been suggested and developed to handle conceptual uncertainty related to mass discharge estimates and capture zone delineation, respectively. These methods are based on simulations using multiple conceptual models.

- The use of multiple conceptual models is a more robust way of coping with the conceptual uncertainties as well as investigating the impact of uncertain input parameters. However, to formulate multiple conceptual models and then to incorporate each of these into a mathematical model and run them can in many cases be a very time consuming process.

6 Conclusions and perspectives

Groundwater contamination from point sources is a widespread problem that can threaten both access to clean drinking water resources and sensitive ecosystems. The costs for investigation and clean-up of the many contaminated sites far exceed the limited resources available and regulators are therefore faced with the challenge of prioritising remediation efforts in order to ensure that the sites posing the greatest risk to groundwater are remediated first. Such prioritisation necessitates the use of risk assessment.

This PhD thesis has investigated available methods for risk assessment of groundwater contamination from point sources at both the local scale and the catchment scale and studied the associated uncertainties. The following key findings have been made:

- Risk assessments of point sources are best carried out using tiered and flexible approaches that allow for site-specific adjustments and can be tailored to the knowledge level and available data. The application of tiered approaches will be stronger if assisted by a quantitative or qualitative appreciation of the uncertainties that reflects the degree of belief in the obtained results.

- A literature review has revealed that most of the existing tools for local scale risk assessment simulate the contaminant transport in the unsaturated zone without accounting for gas-phase processes. It is shown that both gas phase transport and degradation in the unsaturated zone can be incorporated into analytical screening models that are suitable for practical risk assessment.

- Mass discharge estimates are very valuable in risk assessments of point sources and constitute an important input for the catchment scale risk assessment. Based on a literature review, several source zone models describing the relationship between the mass discharge and the remaining source mass have been identified. These models are useful for evaluating the contaminant impact over time and the source longevity. A modular leaching model has been developed that can be adapted to the actual data availability at a site and thus is considered useful for catchment-scale risk assessment purposes.

- A tool for catchment scale risk assessments has been developed. The tool provides an integrated overview of all identified point sources within a catchment and can thereby improve the basis for a risk-based prioritisation of the sites. Catchment scale risk assessment approaches are found to be valuable for: the identification of point sources that are most likely to cause current or future contamination at the receptor (water supply), the identification of unknown point sources in the catchment, and the elucidation of where more information is needed to improve the analysis.

- Risk assessments suffer from data limitations and are prone to large uncertainties. The predictions made in risk assessments can often not be validated against observations and the results therefore depend entirely on the input entered. Forward uncertainty approaches, sensitivity analyses and qualitative approaches are possible options for evaluating the uncertainty in such situations.

- Uncertainty related to the formulation of the conceptual model can significantly influence the risk assessment result at both the local and catchment scale. Acknowledging the conceptual uncertainty, for example through multiple model simulation, is important and can lead to a more robust foundation on which to make decisions. However, the time required to formulate multiple conceptual models and incorporate each of these into a mathematical model may limit the use of such approaches in practice.

- Contaminant mass discharge estimates from point sources at local scale are uncertain. A methodology that uses multiple conceptual site models in a Bayesian inverse geostatistical framework has been developed for quantifying the uncertainty related to mass discharge estimates and local scale risk assessment of groundwater contamination.

- The uncertainties in risk assessment of contaminated sites at catchment scale are primarily related to the mass discharge estimates from the sites within the catchment, the capture zone delineation and the degree of degradation during transport through the catchment. These uncertainties hamper the prioritisation of point sources at catchment scale. It is demonstrated how an assessment of the uncertainties can be incorporated into the prioritisation using a scoring system and how this can lead to an improved foundation for the decision-making in the catchment.

6.1. Future research directions

The work carried out and reported in this PhD thesis has identified a number of areas that should be the subject of further research and investigations:

- **Development and validation of local scale risk assessment models**. Future research is needed on how complex source architectures and presence of free-phase can adequately be conceptualised and accounted for in risk assessment models. The incorporation of fracture transport into local scale models should also be an issue for further research. More research is also suggested for testing and validating the suitability of the simple local scale risk assessment models on field studies and/or by comparison to advanced numerical models.

- **Improvements of catchment scale risk assessment models**. Catchment scale risk assessment models are highly dependent on the groundwater modelling. More research on the effect of alternative geological conceptual models on the delineation of well catchments is of interest. A validation of catchment scale risk assessment models is also an issue for future research.

- **Uncertainty and prioritisation of contaminated sites**. The influence of uncertainty on the prioritisation of contaminated sites should be the target for more research. The robustness of the proposed scoring system should be tested and the sensitivity of the obtained ranking/prioritisation to the assigned scores should be evaluated. Other methods for incorporating uncertainty into the prioritisation of contaminated sites should be investigated, and could for example include Bayesian Belief Networks.

- **Incorporation of environmental economics**. Including environmental economics in catchment scale risk assessments is required in order to address the question of how to best spend the available resources. The incorporation of economics could for example help determine when the costs of collecting additional data to reduce the uncertainties exceed the costs of making a wrong prioritisation (decision) of the sites in the catchment, or when it would be better to clean the abstracted water or move the waterworks.

7 References

Aller, L., Bennett, T., Lehr, J., Petty, H., Hackett, G., 1987. DRASTIC: a standardised system for evaluating groundwater pollution potential using hydrogeologic settings. U.S. EPA, Rep: EPA/600/2-87/035.

Andricevic, R., Cvetkovic, V., 1996. Evaluation of risk from contaminants migrating by groundwater. Water Resources Research 32(3), 611-621.

Annable, M.D., Hatfield, K., Cho, J., Klammler, H., Parker, B.L., Cherry, J.A., Rao, P.S.C., 2005. Field-Scale Evaluation of the Passive Flux Meter for Simultaneous Measurement of Groundwater and Contaminant Fluxes. Environmental Science and Technology 39(18), 7194-7201.

ANPA, 2002. ROME: ReasOnable Maximum Exposure - Operating Manual. National Agency for Protection of the Environment (Agenzia Nazionale Protezione Ambiente).

Arey, J.S., Gschwend, P.M., 2005. A physical-chemical screening model for anticipating widespread contamination of community water supply wells by gasoline constituents. Journal of Contaminant Hydrology 76(1), 109-138.

ASTM, 1999. RBCA Fate and Transport Models: Compendium and Selection Guidance. American Society for Testing and Materials.

Auer, L.H., Rosenberg, N.D., Birdsell, K.H., Whitney, E.M., 1996. The effects of barometric pumping on contaminant transport. Journal of Contaminant Hydrology 24(2), 145-166.

Avagliano, S., Vecchio, A., Belgiorno, V., 2005. Sensitive Parameters In Predicting Exposure Contaminants Concentration In A Risk Assessment Process. Environmental Monitoring and Assessment 111[1-3], 133-148.Kluwer Academic Publishers.

Aziz, C.E., Newell, C.J., Gonzales, J.R., 2000. BIOCHLOR - Natural Attenuation Decision Support System. User's Manual Version 1.0. US Environmental Protection Agency. US Environmental Protection Agency.

Babiker, I.S., Mohamed, M.A.A., Hiyama, T., Kato, K., 2005. A GIS-based DRASTIC model for assessing aquifer vulnerability in Kakamigahara Heights, Gifu Prefecture, central Japan. Science of the Total Environment 345(1-3), 127-140.

Baehr, A.L., Stackelberg, P.E., Baker, R.J., 1999. Evaluation of the atmosphere as a source of volatile organic compounds in shallow groundwater. Water Resources Research 35(1), 127-136.

Bardos, P., Lewis, A., Nortcliff, S., Matiotti, C., Marot, F., Sullivan, T., 2002. Review of Decision Support Tools for Contaminated Land Management, and their Use in Europe. Austrian Federal Environment Agency, on behalf of CLARINET.

Barlebo, H.C., Hill, M.C., Rosbjerg, D., Jensen, K.H., 1998. Concentration data and dimensionality in groundwater models: Evaluation using inverse modelling. Nordic Hydrology 29(3), 149-178.

Basu, N.B., Fure, A.D., Jawitz, J.W., 2008. Simplified contaminant source depletion models as analogs of multiphase simulators. Journal of Contaminant Hydrology 97(3-4), 87-99.

Basu, N.B., Rao, P.S.C., Poyer, I.C., Annable, M.D., Hatfield, K., 2006. Flux-based assessment at a manufacturing site contaminated with trichloroethylene. Journal of Contaminant Hydrology 86[1-2], 105-127.

Batlle-Aguilar, J., Brouyere, S., Dassargues, A., Morasch, B., Hunkeler, D., Hohener, P., Diels, L., Vanbroekhoven, K., Seuntjens, P., Halen, H., 2009. Benzene dispersion and natural attenuation in an alluvial aquifer with strong interactions with surface water. Journal of Hydrology 369(3-4), 305-317.

Baudrit, C., Guyonnet, D., Dubois, D., 2007. Joint propagation of variability and imprecision in assessing the risk of groundwater contamination. Journal of Contaminant Hydrology 93(1-4), 72-84.

Bauer, S., Bayer-Raich, M., Holder, T., Kolesar, C., Muller, D., Ptak, T., 2004. Quantification of groundwater contamination in an urban area using integral pumping tests. Journal of Contaminant Hydrology 75[3], 183-213.

Beland-Pelletier, C., Fraser, M., Barker, J., Bockelmann, A., Ptak, T. Estimating contaminant mass discharge: A comparison of the multilevel point measurement and the integral pumping investigation approaches and their uncertainties. (submitted).

Beven, K., 2002. Towards a coherent philosophy for modelling the environment. Proceedings of the Royal Society A-Mathematical Physical and Engineering Sciences 458(2026), 2465-2484.

Beven, K., 2009b. How to make predictions. In: Beven, K. (Eds.), Environmental Modelling: An Uncertain Future? Routledge, Taylor & Francis Group, London and New York, pp. 1-30.

Beven, K., 2009a. Environmental Modelling: An Uncertain Future? Routledge, Taylor & Francis Group, London and New York.

Beven, K., 2009c. Simulation with no historical data available. In: Beven, K. (Eds.), Environmental Modelling: An Uncertain Future? Routledge, Taylor & Francis Group, London and New York.

Beven, K., 2005. On the concept of model structural error. Water Science and Technology 52[6], 167-175.

Beven, K., Binley, A., 1992. The Future of Distributed Models - Model Calibration and Uncertainty Prediction. Hydrological Processes 6(3), 279-298.

Beven, K.J., Smith, P.J., Freer, J.E., 2008. So just why would a modeller choose to be incoherent? Journal of Hydrology 354(1-4), 15-32.

Bjerg, P.L., Tuxen, N., Reitzel, L.A., Albrechtsen, H., Kjeldsen, P., 2009. Natural Attenuation Processes in Landfill Leachate Plumes at Three Danish Sites. Ground Water Early View.

Blasone, R.S., 2007. Parameter Estimation and Uncertainty Asessment in Hydrological Modelling. PhD thesis, Institute of Environment and Resources, Technical University of Denmark.
Bobba, A.G., Singh, V.P., Bengtsson, L., 1995. Application of uncertainty analysis to groundwater pollution modeling. Environmental Geology 26[2].

Bockelmann, A., Ptak, T., Teutsch, G., 2001. An analytical quantification of mass fluxes and natural attenuation rate constants at a former gasworks site. Journal of Contaminant Hydrology 53[3-4], 429-453.

Bockelmann, A., Zamfirescu, D., Ptak, T., Grathwohl, P., Teutsch, G., 2003. Quantification of mass fluxes and natural attenuation rates at an industrial site with a limited monitoring network: a case study. Journal of Contaminant Hydrology 60[1-2], 97-121.

Bojorquez-Tapia, L.A., Cruz-Bello, G.M., Luna-Gonzalez, L., Juarez, L., Ortiz-Perez, M.A., 2009. V-DRASTIC: Using visualization to engage policymakers in groundwater vulnerability assessment. Journal of Hydrology 373(1-2), 242-255.

Bredehoeft, J., 2005. The conceptualization model problem - surprise. Hydrogeology Journal 13[1], 37-46.Springer-Verlag

Brooks, M.C., Wood, A.L., Annable, M.D., Hatfield, K., Cho, J., Holbert, C., Rao, R.S.C., Enfield, C.G., Lynch, K., Smith, R.E., 2008. Changes in contaminant mass discharge from DNAPL source mass depletion: Evaluation at two field sites. Journal of Contaminant Hydrology 102(1-2), 140-153.

Brown, J.D., 2004. Knowledge, uncertainty and physical geography: towards the development of methodologies for questioning belief. Transactions of the Institute of British Geographers 29(3), 367-381.

Brown, J.D., Heuvelink, G.B.M., 2007. The Data Uncertainty Engine (DUE): A software tool for assessing and simulating uncertain environmental variables. Computers & Geosciences 33(2), 172-190.

Capital Region of Denmark, 2009. Risk-based prioritisation of point sources in the focus area for Birkerød Waterworks. Composed by Orbicon A/S for the Captial Region of Denmark (in Danish).

Capital Region of Denmark, Region Zealand, 2010. Koncept for RIsk-based Prioritisation of Point sources (KRIPP). Version 1.1. In: Kjærsgaard, P., Tuxen, N., Overheu, N. D., Nielsen, S., and Christensen, S. B. Composed by Orbicon A/S for the Captial Region of Denmark (in Danish).

Carle, S.F., Fogg, G.E., 1997. Modeling spatial variability with one and multidimensional continuous-lag Markov chains. Mathematical Geology 29(7), 891-918.

Chambon, J., Bjerg, P.L. and Binning, P.J. (2010). A risk assessment tool for contaminated sites in low-permeability fractured media. Miljøstyrelsens Teknologiprogram for jord- og grundvandsforurening.(in press)

Chisala, B.N., Tait, N.G., Lerner, D.N., 2007. Evaluating the risks of methyl tertiary butyl ether (MTBE) pollution of urban groundwater. Journal of Contaminant Hydrology 91[1-2], 128-145.

Christ, J.A., Ramsburg, C.A., Pennell, K.D., Abriola, L.M., 2006. Estimating mass discharge from dense nonaqueous phase liquid source zones using upscaled mass transfer coefficients: An evaluation using multiphase numerical simulations. Water Resources Research 42(11).

Christensen, F.M., Andersen, O., Duijm, N.J., Harremoes, P., 2003. Risk terminology - A platform for common understanding and better communication. Journal of Hazardous Materials 103[3], 181-203.

Christophersen, M., Broholm, M.M., Mosbaek, H., Karapanagioti, H.K., Burganos, V.N., Kjeldsen, P., 2005. Transport of hydrocarbons from an emplaced fuel source experiment in the vadose zone at Airbase V ae rlose, Denmark. Journal of Contaminant Hydrology 81(1-4), 1-33.

Conant, B., Cherry, J.A., Gillham, R.W., 2004. A PCE groundwater plume discharging to a river: influence of the streambed and near-river zone on contaminant distributions. Journal of Contaminant Hydrology 73(1-4), 249-279.

Conant, B.H., Gillham, R.W., Mendoza, C.A., 1996. Vapor transport of trichloroethylene in the unsaturated zone: Field and numerical modeling investigations. Water Resources Research 32(1), 9-22.

Connell, L.D., 2002. A simple analytical solution for unsaturated solute migration under dynamic water movement conditions and root zone effects. Sustainable Groundwater Development 193, 255-264.

Cushman, D.J., Driver, K.S., Ball, S.D., 2001. Risk assessment for environmental contamination: an overview of the fundamentals and application of risk assessment at contaminated sites. Canadian Journal of Civil Engineering 28[1], 155-162. NRC Research Press.

Cypher, J.A., Lemke, L.D., 2009. Multiple Working Transport Hypotheses in a Heterogeneous Glacial Aquifer System. Ground Water Monitoring and Remediation 29(3), 105-119.

Dakhel, N., Pasteris, G., Werner, D., Hohener, P., 2003. Small-volume releases of gasoline in the Vadose Zone: Impact of the additives MTBE and ethanol on groundwater quality. Environmental Science & Technology 37(10), 2127-2133.

Danish EPA, 2002. Guidelines on Remediation of Contaminated Sites. Environmental Guidelines 7. Danish Ministry of the Environment.

Danish EPA, 1998. Remediation of Contaminated Sites. Environmental Guidelines Nr. 6. Danish Ministry of the Environment (in Danish).

Danish Regions, 2007. Documentation report. GISP - Prioritisation system for mapped contaminated sites. Danish Regions.

Davison, A., Howard, G., Stevens, M., Calla, P., Kirby, R., Deere, D., Bartram, J., 2004. Water safety plans - Managing drinking-water quality from catchment to consumer. World Health Organisation (WHO).

Davison, R., Hall, D.H., 2003. ConSim Version 2. User Manual. Golder Associates and UK Environment Agency. Golder Associates.

Davison, R.M., Prabnarong, P., Whittaker, J.J., Lerner, D.N., 2002. A probabilistic management system to optimize the use of urban groundwater. Sustainable Groundwater Development 193, 265-276.

De Jonge, H., Rothenberg, G., 2005. New device and method for flux-proportional sampling of mobile solutes in soil and groundwater. Environmental Science & Technology 39(1), 274-282.

DeVaull, G., Ettinger, R., Gustafson, J., 2002. Chemical vapor intrusion from soil or groundwater to indoor air: Significance of unsaturated zone biodegradation of aromatic hydrocarbons. Soil and Sediment Contamination 11[4], 625-641.

DiFilippo, E.L., Brusseau, M.L., 2008. Relationship between mass-flux reduction and source-zone mass removal: Analysis of field data. Journal of Contaminant Hydrology 98(1-2), 22-35.

Ditlevsen, O., Madsen, H. O., 1996. Structural Reliability Methods. John Wiley & Sons, Chichester, UK. Internet Edition 2.3.7. July-September 2007. http://www.web.mek.dtu.dk/staff/od/books.htm.

Doherty, J., 2005. PEST: software for model-independent parameter estimation. Water Mark Numerical Computing, Australia.

EA, 2004. Model Procedures for the Management of Land Contamination. UK Environment Agency, Contaminated Land Report 11.

EC, 2006. Soil protection - The story behind the Strategy. European Commission

EEA, 2007. CSI 015 - Progress in management of contaminated sites. European Environment Agency.

Einarson, M.D., Mackay, D.M., 2001. Predicting impacts of groundwater contamination. Environmental Science and Technology 35[3], 66A-73A.ACS.

Enzenhoefer, R., Nowak, W., and Helmig, R., 2010. Using probabilistic well vulnerability criteria for a risk-based preventive drinking water safety concept. Proceedings of Groundwater Quality 2010, Zurich, Switzerland.

European Commission, 2000. Directive 2000/60/EC. Establishing a framework for community action in the field of water policy, 2000.

Falta, R.W., Basu, N., Rao, P.S., 2005a. Assessing impacts of partial mass depletion in DNAPL source zones: II. Coupling source strength functions to plume evolution. Journal of Contaminant Hydrology 79[1-2], 45-66.

Falta, R.W., Javandel, I., Pruess, K., Witherspoon, P.A., 1989. Density-driven flow of gas in the unsaturated zone due to the evaporation of volatile organic compounds. Water Resources Research 25[10], 2159-2169.

Falta, R.W., 2008. Methodology for comparing source and plume remediation alternatives. Ground Water 46[2], 272-285.

Falta, R.W., Suresh Rao, P., Basu, N., 2005b. Assessing the impacts of partial mass depletion in DNAPL source zones: I. Analytical modeling of source strength functions and plume response. Journal of Contaminant Hydrology 78[4], 259-280.

Feenstra, S., Cherry, J.A., Parker, B.L., 1996. Conceptual Models for the Behaviour of Dense Non-Aqueous Phase Liquids (DNAPLs) in the subsurface. In: Pankow, J.F., Cherry J.A. (Eds.), Dense Chlorinated Solvents and other DNAPLs in Groundwater. Waterloo Press, pp. 53-88.

Ferguson, C., Darmendrail, D., Freier, K., Jensen, B. K., Jensen, J., Kasanas, H., Urzelai, A., Vegter, J. e., 1998. Risk Assessment for Contaminated Sites in Europe. Scientific Basis, LQM Press, Nottingham, Volume 1.

Feyen, L., Beven, K.J., De Smedt, F., Freer, J., 2001. Stochastic capture zone delineation within the generalized likelihood uncertainty estimation methodology: Conditioning on head observations. Water Resources Research 37[3], 625-638.American Geophysical Union.

Feyen, L., Gomez-Hernindez, J.J., Ribeiro Jr, P.J., Beven, K.J., Smedt, F.D., 2003. A Bayesian approach to stochastic capture zone delineation incorporating tracer arrival times, conductivity measurements, and hydraulic head observations. Water Resources Research 39[5].

Fraser, M., Barker, J.F., Butler, B., Blaine, F., Joseph, S., Cooke, C., 2008. Natural attenuation of a plume from an emplaced coal tar creosote source over 14 years. Journal of Contaminant Hydrology 100(3-4), 101-115.

Freeze, R.A., Massmann, J., Smith, L., Sperling, T., James, B., 1990. Hydrogeological decision analysis. 1. A framework. Ground Water 28[5], 738-766.

Frind, E.O., Molson, J.W., Rudolph, D.L., 2006. Well Vulnerability: A Quantitative Approach for Source Water Protection. Ground Water 44[5], 732-742.

Frind, E.O., Muhammad, D.S., Molson, J.W., 2002. Delineation of Three-Dimensional Well Capture Zones for Complex Multi-Aquifer Systems. Ground Water 40[6], 586.

Fure, A.D., Jawitz, J.W., Annable, M.D., 2006. DNAPL source depletion: Linking architecture and flux response. Journal of Contaminant Hydrology 85(3-4), 118-140.

Gaganis, P., Smith, L., 2008. Accounting for model error in risk assessments: Alternatives to adopting a bias towards conservative risk estimates in decision models. Advances in Water Resources 31(8), 1074-1086.

Guyonnet, D., Come, B., Perrochet, P., Parriaux, A., 1999. Comparing two methods for addressing uncertainty in risk assessments. Journal of Environmental Engineering 125[7], 660-665.

Hamed, M.M., Bedient, P.B., Conte, J.P., 1996a. Numerical stochastic analysis of groundwater contaminant transport and plume containment. Journal of Contaminant Hydrology 24(1), 1-24.

Hamed, M.M., Bedient, P.B., Dawson, C.N., 1996b. Probabilistic modeling of aquifer heterogeneity using reliability methods. Advances in Water Resources 19(5), 277-295.

Hamed, M.M., Conte, J.P., Bedient, P.B., 1995. Probabilistic Screening Tool for Ground-Water Contamination Assessment. Journal of Environmental Engineering 121[11], 767-775.

Hamed, M.M., El-Beshry, M.Z., 2006. Application of first-order reliability method to modelling the fate and transport of benzene in groundwater. International Journal of Environment and Pollution 26[4], 327-346.

Hatfield, K., Annable, M., Cho, J., Rao, P.S.C., Klammler, H., 2004. A direct passive method for measuring water and contaminant fluxes in porous media. Journal of Contaminant Hydrology 75[3-4], 155-181.

Helweg, A., 2000. Pesticides. In: Helweg, A. (Eds.), Chemicals in the environment (in Danish). Gads Forlag, pp. 66-94.

Herold, M., Ptak, T., Bayer-Raich, M., Wendel, T., Grathwohl, P., 2009. Integral quantification of contaminant mass flow rates in a contaminated aquifer: Conditioning of the numerical inversion of concentration-time series. Journal of Contaminant Hydrology 106(1-2), 29-38.

Heuvelink, G.B.M., Brown, J.D., van Loon, E.E., 2007. A probabilistic framework for representing and simulating uncertain environmental variables. International Journal of Geographical Information Science 21(5), 497-513.

Hill, M. C., Tiedeman, C. R., 2007. Effective Groundwater Calibration. Wiley: Hoboken, NJ.

Hoeting, J.A., Madigan, D., Raftery, A.E., Volinsky, C.T., 1999. Bayesian model averaging: A tutorial. Statistical Science 14(4), 382-401.

Hohener, P., Dakhel, N., Christophersen, M., Broholm, M., Kjeldsen, P., 2006. Biodegradation of hydrocarbons vapors: Comparison of laboratory studies and field investigations in the vadose zone at the emplaced fuel source experiment, Airbase Vaerlose, Denmark. Journal of Contaminant Hydrology 88(3-4), 337-358.

Højberg, A.L., Refsgaard, J.C., 2005. Model uncertainty - Parameter uncertainty versus conceptual models. Water Science and Technology 52[6], 177-186.

Jarsjö, J., Bayer-Raich, M., Ptak, T., 2005. Monitoring groundwater contamination and delineating source zones at industrial sites: Uncertainty analyses using integral pumping tests. Journal of Contaminant Hydrology 79[3-4], 107-134.

Jawitz, J.W., Annable, M.D., Demmy, G.G., Rao, P.S.C., 2003. Estimating nonaqueous phase liquid spatial variability using partitioning tracer higher temporal moments. Water Resources Research 39(7).

Jawitz, J.W., Fure, A.D., Demmy, G.G., Berglund, S., Rao, P.S.C., 2005. Groundwater contaminant flux reduction resulting from nonaqueous phase liquid mass reduction. Water Resources Research 41[10], W10408-1.

Jury, W.A., Spencer, W.F., Farmer, W.J., 1983. Behavior assessment model for trace organics in soil: I. Model description. Journal of Environmental Quality 12[4], 558-564.

Kalbus, E., Schmidt, C., Bayer-Raich, M., Leschik, S., Reinstorf, F., Balcke, G.U., Schirmer, M., 2007. New methodology to investigate potential contaminant mass fluxes at the stream-aquifer interface by combining integral pumping tests and streambed temperatures. Environmental Pollution 148[3], 808-816.

Kamath, R. K., Newell, C. J., Looney, B. B., Vangelas, K. M., Adamson, D. T., 2006. BIOBALANCE: A mass balance toolkit. For evaluating source depletion, competition effects, long-term sustainability, and plume dynamics. User's Manual. Groundwater Services Inc.

Kao, C.M., Wang, Y.S., 2001. Field investigation of the natural attenuation and intrinsic biodegradation rates at an underground storage tank site. Environmental Geology 40[4-5], 622-631.

Karapanagioti, H.K., Gaganis, P., Burganos, V.N., 2003. Modeling attenuation of volatile organic mixtures in the unsaturated zone: codes and usage. Environmental Modelling and Software 18[4], 329-337.

Kennedy, C.A., Lennox, W.C., 1999. Screening model for the contamination of a well in a uniform flow field. Water Resources Research 35[9], 2871-2875.American Geophysical Union.

King, M.W.G., Barker, J.F., Devlin, J.F., Butler, B.J., 1999. Migration and natural fate of a coal tar creosote plume - 2. Mass balance and biodegradation indicators. Journal of Contaminant Hydrology 39[3-4], 281-307.

Konikow, L.F., Bredehoeft, J.D., 1992. Groundwater Models Cannot be Validated. Advances in Water Resources 15(1), 75-83.

Kubert, M., Finkel, M., 2006. Contaminant mass discharge estimation in groundwater based on multi-level point measurements: A numerical evaluation of expected errors. Journal of Contaminant Hydrology 84(1-2), 55-80.

Kumar, V., Schuhmacher, M., Garcia, M., 2006. Integrated fuzzy approach for system modeling and risk assessment.

Lahvis, M.A., Baehr, A.L., Baker, R.J., 1999. Quantification of aerobic biodegradation and volatilization rates of gasoline hydrocarbons near the water table under natural attenuation conditions. Water Resources Research 35(3), 753-765.

Lemke, L., Bahrou, A., 2009. Partitioned multiobjective risk modeling of carcinogenic compounds in groundwater. Stochastic Environmental Research and Risk Assessment 23(1), 27-39.

Lemming, G., Friis-Hansen, P., Bjerg, P.L., 2010. Risk-based economic decision analysis of remediation options at a PCE-contaminated site. Journal of Environmental Management 91(5), 1169-1182.

Mantovan, P., Todini, E., 2006. Hydrological forecasting uncertainty assessment: Incoherence of the GLUE methodology. Journal of Hydrology 330(1-2), 368-381.

Matott, L.S., Babendreier, J.E., Purucker, S.T., 2009. Evaluating uncertainty in integrated environmental models: A review of concepts and tools. Water Resources Research 45.

McDonald, M.G., Harbaugh, A.W., 1988. A modular three-dimensional finite-difference ground-water flow model: U.S. Geological Survey Techniques of Water Resources Investigations. Modelling Techniques Book 6, Chapt. A1. US Geological Survey.

McGuire, T.M., Mcdade, J.M., Newell, C.J., 2006. Performance of DNAPL source depletion technologies at 59 chlorinated solvent-impacted sites. Ground Water Monitoring and Remediation 26(1), 73-84.

McKnight, U.S., Funder, S.G., Rasmussen, J.J., Finkel, M., Binning, P.J., Bjerg, P.L., 2010. An integrated model for assessing the risk of TCE groundwater contamination to human receptors and surface water ecosystems. Ecological Engineering (in press).

Mendoza, C.A., Frind, E.O., 1990. Advective-Dispersive Transport of Dense Organic Vapors in the Unsaturated Zone .1. Model Development. Water Resources Research 26(3), 379-387.

Morris, M.D., 1991. Factorial Sampling Plans for Preliminary Computational Experiments. Technometrics 33(2), 161-174.

Neuman, S.P., 2002. Accounting for conceptual model uncertainty via maximum likelihood Bayesian model averaging. IAHS-AISH Publication [277], 303-313.

Neuman, S. P., Wierenga, P. J., 2003. A comprehensive strategy of hydrogeologic modeling and analysis for nuclear facilities and sites. University of Arizona, Rep. NUREG/CR-6805.

Newell, C.J., Cowie, I., McGuire, T.M., Mcnab, W.W., 2006. Multiyear temporal changes in chlorinated solvent concentrations at 23 monitored natural attenuation sites. Journal of Environmental Engineering-Asce 132(6), 653-663.

Newell, C.J., McLeod, R.K., Gonzales, J.R., 1996. BIOSCREEN - Natural Attenuation Decision Support System. User's Manual Version 1.4. US Environmental Protection Agency. US Environmental Protection Agency.

Nichols, E.M., 2004. In a state of (mass) flux. Ground Water Monitoring and Remediation 24(3).

Nobre, R.C.M., Rotunno, O.C., Mansur, W.J., Nobre, M.M.M., Cosenza, C.A.N., 2007. Groundwater vulnerability and risk mapping using GIS, modeling and a fuzzy logic tool. Journal of Contaminant Hydrology 94(3-4), 277-292.

Park, E., Parker, J.C., 2005. Evaluation of an upscaled model for DNAPL dissolution kinetics in heterogeneous aquifers. Advances in Water Resources 28[12], 1280-1291.

Parker, J.C., 2003. Physical processes affecting natural depletion of volatile chemicals in soil and groundwater. Vadose Zone Journal 2(2), 222-230.

Parker, J.C., Park, E., 2004. Modeling field-scale dense nonaqueous phase liquid dissolution kinetics in heterogeneous aquifers. Water Resources Research 40[5.

Pasteris, G., Werner, D., Kaufmann, K., Hohener, P., 2002. Vapor phase transport and biodegradation of volatile fuel compounds in the unsaturated zone: A large scale lysimeter experiment. Environmental Science & Technology 36(1), 30-39.

Pollard, S.J., Yearsley, R., Reynard, N., Meadowcroft, I.C., Duarte-Davidson, R., Duerden, S.L., 2002. Current directions in the practice of environmental risk assessment in the United Kingdom. Environmental Science & Technology 36(4), 530-538.

Ravi, V., Johnson, J. A., 1997. VLEACH - A One-Dimensional Finite Defference Vadose Zone Leaching Model. Version 2.2. U.S. EPA Robert S. Kerr Environmental reseach Laboratory, Ada OK.

Refsgaard, J.C., van der Sluijs, J.P., Brown, J., van der Keur, P., 2006. A framework for dealing with uncertainty due to model structure error. Advances in Water Resources 29[11], 1586-1597.

Refsgaard, J.C., van der Sluijs, J.P., Højberg, A.L., Vanrolleghem, P.A., 2007. Uncertainty in the environmental modelling process - A framework and guidance. Environmental Modelling and Software 22[11], 1543-1556.

Region Zealand, 2010. Risk assessment and prioritisation of point sources in Haslev. Composed by Orbicon A/S for Region Zealand (in Danish).

Reilly, T.E., Pollock, D.W., 1996. Sources of water to wells for transient cyclic systems. Ground Water 34(6), 979-988.

Riva, M., Guadagnini, L., Guadagnini, A., Ptak, T., Martac, E., 2006. Probabilistic study of well capture zones distribution at the Lauswiesen field site. Journal of Contaminant Hydrology 88(1-2), 92-118.

Rojas, R., Feyen, L., Dassargues, A., 2008. Conceptual model uncertainty in groundwater modeling: Combining generalized likelihood uncertainty estimation and Bayesian model averaging. Water Resources Research 44(12).

Rojas, R., Feyen, L., Dassargues, A., 2009. Sensitivity analysis of prior model probabilities and the value of prior knowledge in the assessment of conceptual model uncertainty in groundwater modelling. Hydrological Processes 23(8), 1131-1146.

Royal Society, 1992. Risk: Analysis, Perception and Management. Report of a Royal Society Study Group. The Royal Society, London.

Rupert, M.G., 2001. Calibration of the DRASTIC ground water vulnerability mapping method. Ground Water 39(4), 625-630.

Saltelli, A., Chan, K., Scott, M., 2000. Sensitivity Analysis. John Wiley & Sons, New York.

Saltelli, A., Ratto, M., Tarantola, S., Campolongo, F., 2006. Sensitivity analysis practices: Strategies for model-based inference. Reliability Engineering & System Safety 91(10-11), 1109-1125.

Secunda, S., Collin, M.L., Melloul, A.J., 1998. Groundwater vulnerability assessment using a composite model combining DRASTIC with extensive agricultural land use in Israel's Sharon region. Journal of Environmental Management 54(1), 39-57.

Shan, C., Stephens, D.B., 1995. An Analytical Solution for Vertical Transport of Volatile Chemicals in the Vadose Zone. Journal of Contaminant Hydrology 18(4), 259-277.

Sobol, I.M., 2001. Global sensitivity indices for nonlinear mathematical models and their Monte Carlo estimates. Mathematics and Computers in Simulation 55(1-3), 271-280.

Soga, K., Page, J.W.E., Illangasekare, T.H., 2004. A review of NAPL source zone remediation efficiency and the mass flux approach. Journal of Hazardous Materials 110[1-3], 13-27.

Sohn, M.D., Small, M.J., Pantazidou, M., 2000. Reducing uncertainty in site characterization using Bayes Monte Carlo methods. Journal of Environmental Engineering 126[10], 893-902. ASCE.

Somaratne, N. and Ashman, G., 2007. Risk-based approach to groundwater and wellfield protection in South Australia. Proceedings of Groundwater Quality 2007, Fremantle, Western Australia, pp. 383.

Sonnenborg, T.O., Engesgaard, P., Rosbjerg, D., 1996. Contaminant transport at a waste residue deposit .1. Inverse flow and nonreactive transport modeling. Water Resources Research 32(4), 925-938.

Spear, R.C., Hornberger, G.M., 1980. Eutrophication in Peel Inlet .2. Identification of Critical Uncertainties Via Generalized Sensitivity Analysis. Water Research 14(1), 43-49.

Spence, L.R., 2001. RISC4. User's Manual. Spence Engineering and BP Oil ltd. Spence Engineering and BP Oil ltd.

Stauffer, F., Guadagnini, A., Butler, A., Franssen, H.J.H., Wiel, N.V.D., Bakr, M., Riva, M., Guadagnini, L., 2005. Delineation of Source Protection Zones Using Statistical Methods. Water Resources Management 19[2], 163-185.Kluwer Academic Publishers.

Stedinger, J.R., Vogel, R.M., Lee, S.U., Batchelder, R., 2008. Appraisal of the generalized likelihood uncertainty estimation (GLUE) method. Water Resources Research 44.

Strebelle, S., 2002. Conditional simulation of complex geological structures using multiple-point statistics. Mathematical Geology 34(1), 1-21.

Sudicky, E.A., Frind, E.O., 1982. Contaminant Transport in Fractured Porous-Media - Analytical Solutions for A System of Parallel Fractures. Water Resources Research 18(6), 1634-1642.

Sudicky, E.A., Frind, E.O., 1984. Contaminant Transport in Fractured Porous-Media - Analytical Solution for A 2-Member Decay Chain in A Single Fracture. Water Resources Research 20(7), 1021-1029.

Suthersan, S., Divine, C., Quinnan, J., Nichols, E., 2010. Flux-Informed Remediation Decision Making. Ground Water Monitoring and Remediation 30(1), 36-45.

Tait, N.G., Davison, R.M., Leharne, S.A., Lerner, D.N., 2008. Borehole Optimisation System (BOS) - A case study assessing options for abstraction of urban groundwater in Nottingham, UK. Environmental Modelling & Software 23(5), 611-621.

Tait, N.G., Davison, R.M., Whittaker, J.J., Leharne, S.A., Lerner, D.N., 2004a. Borehole Optimisation System (BOS) - A GIS based risk analysis tool for optimising the use of urban groundwater. Environmental Modelling and Software 19[12], 1111-1124.

Tait, N.G., Lerner, D.N., Smith, J.W.N., Leharne, S.A., 2004b. Prioritisation of abstraction boreholes at risk from chlorinated solvent contamination on the UK Permo-Triassic Sandstone aquifer using a GIS. Science of the Total Environment 319[1-3], 77-98.

Thornton, S.F., Lerner, D.N., Banwart, S.A., 2001. Assessing the natural attenuation of organic contaminants in aquifers using plume-scale electron and carbon balances: model development with analysis of uncertainty and parameter sensitivity. Journal of Contaminant Hydrology 53(3-4), 199-232.

Tiedeman, C., Gorelick, S.M., 1993. Analysis of Uncertainty in Optimal Groundwater Contaminant Capture Design. Water Resources Research 29(7), 2139-2153.

Troldborg, L., Refsgaard, J.C., Jensen, K.H., Engesgaard, P., 2007. The importance of alternative conceptual models for simulation of concentrations in a multi-aquifer system. Hydrogeology Journal 15[5], 843-860.Springer-Verlag.

Troldborg, M., Nowak, W., Binning, P. J., Bjerg, P. L., Helmig, R., 2010. Uncertainty of mass discharge estimates from contaminated sites using a fully Bayesian framework. IAHS Red Book publication. ModelCARE2009 Wuhan, China.

Tuxen, N., Larsen, L. C., Troldborg, M., Binning, P. J., Bjerg, P. L., 2008. Re-evaluation of existing investigations, Rundforbivej 176 (in Danish). Region Hovedstaden, Orbicon A/S.

Tuxen, N., Troldborg, M., Binning, P. J., Kjeldsen, P., Bjerg, P. L., 2006. Risk assessment of point sources (RAP). Københavns Amt, Institute of Environment

& Resources, Technical University of Denmark, Available at http://sara.er.dtu.dk/ (in Danish).

Tuxen, N., Ejlskov, P., Albrechtsen, H.J., Reitzel, L.A., Pedersen, J.K., Bjerg, P.L., 2003. Application of Natural Attenuation to Ground Water Contaminated by Phenoxy Acid Herbicides at an Old Landfill in Sjoelund, Denmark. Ground Water Monitoring and Remediation 23[4], 48-58.

Unlu, K., Parker, J.C., Chong, P.K., 1995. Comparison of three uncertainty-analysis methods to assess impacts on groundwater of constituents leached from land-disposed waste. Hydrogeology Journal 3(2).

Unlu, K., Kemblowski, M.W., Parker, J.C., Stevens, D., Chong, P.K., Kamil, I., 1992. A Screening Model for Effects of Land-Disposed Wastes on Groundwater Quality. Journal of Contaminant Hydrology 11(1-2), 27-49.

US EPA, 2003. The DNAPL Remediation Challenge: Is There a Case for Source Depletion? Expert Panel on DNAPL remediation. In: Kavanaugh, M. C. and Rao, P. S. C. National Risk Management Research Laboratory, Office of Research and Development. US Environmental Protection Agency, EPA/600/R-03/143.

US EPA, 2010. Website: http://epa.gov/riskassessment/basicinformation.htm#arisk (accessed April 16 2010).

Vassolo, S., Kinzelbach, W., Schaefer, W., 1998. Determination of a well head protection zone by stochastic inverse modelling. Journal of Hydrology (Amsterdam) 206[3-4], 268-280.

Volkova, E., Iooss, B., Van Dorpe, F., 2008. Global sensitivity analysis for a numerical model of radionuclide migration from the RRC "Kurchatov Institute" radwaste disposal site. Stochastic Environmental Research and Risk Assessment 22(1), 17-31.

von Krauss, M.K., Van Asselt, M.B.A., Henze, M., Ravetz, J., Beck, M.B., 2005. Uncertainty and precaution in environmental management. Water Science and Technology 52(6), 1-9.

von Krauss, M.P.K., 2005. Uncertainty in policy relevant sciences. PhD thesis, Institute of Environment and Resources, Technical University of Denmark.

von Krauss, M.P.K., Janssen, P.H.M., 2005. Using the W&H integrated uncertainty analysis framework with non-initiated experts. Water Science and Technology 52(6), 145-152.

Walden, T., 2005. Risk Assessment in Soil Pollution: Comparison Study. Reviews in Environmental Science and Bio/Technology 4[3], 87-113.Kluwer Academic Publishers.

Walker, W.E., Harremoës, P., Rotmans, J., van der Sluijs, J.P., Van Asselt, M.B.A., Janssen, P., Krayer von Krauss, M.P., 2003. Defining uncertainty. A conceptual basis for uncertainty management in model-based decision support. Integrated Assessment 4[1], 5-17.

Weissmann, G.S., Carle, S.F., Fogg, G.E., 1999. Three dimensional hydrofacies modeling based on soil surveys and transition probability geostatistics. Water Resources Research 35(6), 1761-1770.

Worrall, F., Besien, T., 2005. The vulnerability of groundwater to pesticide contamination estimated directly from observations of presence or absence in wells. Journal of Hydrology 303(1-4), 92-107.

Worrall, F., Kolpin, D.W., 2003. Direct assessment of groundwater vulnerability from single observations of multiple contaminants. Water Resources Research 39(12).

Yeh, W.W.G., 1986. Review of Parameter-Identification Procedures in Groundwater Hydrology - the Inverse Problem. Water Resources Research 22(2), 95-108.

Zadeh, L.A., 2005. Toward a generalized theory of uncertainty (GTU) - an outline. Information Sciences 172(1-2), 1-40.

Zhang, K.J., Li, H., Achari, G., 2009. Fuzzy-stochastic characterization of site uncertainty and variability in groundwater flow and contaminant transport through a heterogeneous aquifer. Journal of Contaminant Hydrology 106(1-2), 73-82.

Zhu, J., Sykes, J.F., 2004. Simple screening models of NAPL dissolution in the subsurface. Journal of Contaminant Hydrology 72[1-4], 245-258.

8 Appendices

I. Troldborg, M., Lemming, G., Binning, P.J., Tuxen, N., Bjerg, P.L. (2008). Risk assessment and prioritisation of contaminated sites on the catchment scale. Journal of Contaminant Hydrology 101(1-4), 14-28.

II. Troldborg, M., Binning, P.J., Nielsen, S., Kjeldsen, P. Christensen, A.G. (2009). Unsaturated zone leaching models for assessing risk to groundwater of contaminated sites. Journal of Contaminant Hydrology 105, 28-37.

III. Troldborg, M., Nowak, W., Tuxen, N., Binning, P.J., Bjerg, P.L., Helmig, R. (2010). Uncertainty evaluation of mass discharge estimates from a contaminated site using a fully Bayesian framework. Water Resources Research (in revision).

IV. Overheu, N., Troldborg, M., Tuxen, N., Flyvbjerg, J., Østergaard, H., Jensen, C.B., Binning, P.J., Bjerg, P.L. (2010). Concept for risk-based prioritisation of point sources. Proceedings of Groundwater Quality 2010. Zurich, Switzerland.

Please note that the papers are not included in this web-version but can be obtained from the library at Department of Environmental Engineering, DTU, Miljoevej, Building 113, DK-2800 Kgs. Lyngby, Denmark, library@env.dtu.dk.

The Department of Environmental Engineering (DTU Environment) conducts science-based engineering research within four themes:
Water Resource Engineering, Urban Water Engineering,
Residual Resource Engineering and Environmental Chemistry & Microbiology.
Each theme hosts two to five research groups.

The department dates back to 1865, when Ludvig August Colding, the founder of the department, gave the first lecture on sanitary engineering as response to the cholera epidemics in Copenhagen in the late 1800s.

DTU Environment
Department of Environmental Engineering
Technical University of Denmark

Miljoevej, building 113
DK-2800 Kgs. Lyngby
Denmark

Phone: +45 4525 1600
Fax: +45 4593 2850
e-mail: reception@env.dtu.dk
www.env.dtu.dk

ISBN 978-87-92654-05-2